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THERMAL EXPANSION DATA OF SOME ALKALI ALUMINOSILICATE GLASSES AND THEIR RESPECTIVE GLASS-CERAMICS

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ABSTRACT

The thermal expansion coefficient (α) of several sets of silicate glasses and their respective glass-ceramics have been measured at different temperatures using a fused-silica dilatometer. The glass compositions are based on the $Li_2O-MgO-SiO_2$ system in which MgO and Li_2O were partially replaced by CaO and Al_2O_3, respectively.

The expansion coefficients of the glasses gradually increase with the increase in CaO/MgO replacement, while on the addition of Al_2O_3 instead of Li_2O, the α-values were markedly decreased. The change in the expansion coefficient of the glass with the increase in the added oxide content was discussed in relation to the mode of vibration of the atoms (or groups) in the network, the polarization of the ions and the ability of some cations to build glass-forming units.

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

INTRODUCTION

Practically, a most important, often decisive feature is the value of the linear coefficient of thermal expansion of materials. The thermal expansion of glass and crystalline materials is of prime importance to such considerations as sealing, and where thermal stress and thermal shock resistance are involved.

The anharmonicity of the vibrations of atoms is responsible for the fact that the volume of a solid changes with temperature, i.e., with the amplitude of the vibrations. Thermal expansivity is a complex property connected with the magnitude and distribution of forces acting on the system, and reflects any change of the distribution of forces with increasing thermal vibrations [1].

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The thermal expansion of a glass is primarily related to its composition, thermal history and internal structure, because of its sensitivity to the number and size of the building unit aggregate [2,3]. The presence of more asymmetrical units in the glass will lead to an increase in the thermal expansion coefficient, while a more coherent network will lead to a decrease in this property [4]. Thermal expansion is one of the few techniques providing valuable information regarding structural changes induced by composition modification or heat treatment.

The thermal expansion coefficient of crystalline glass materials (glass-ceramics) is generally quite different from that of their respective parent glasses [5]. Glass-ceramics are remarkable for the very wide range of thermal expansion coefficients which can be obtained. At one extreme, materials having zero or even negative coefficients of thermal expansion are possible while, at the other extreme, materials having expansion coefficients close to those of useful metals are available [5]. It was found to be dependent on the nature of the associated crystalline phases and the content of glassy phase present in the material.

The purpose of this paper is to report the thermal expansion characteristics of some silicate glasses and their respective glass-ceramic materials based on the Li_2O–MgO–SiO_2 system, and to detect the effect of introducing CaO and Al_2O_3 instead of MgO and Li_2O, respectively, on this property.

EXPERIMENTAL

The effect of CaO/MgO and/or Al_2O_3/Li_2O replacement has been investigated on the thermal expansion coefficients (α-values) of the glasses based on the 23.12 Li_2O–13.28 MgO–63.6 SiO_2 (mol%) eutectic glass composition. CaO was introduced in various proportions, such as, 25, 50, 75 and 100%, to replace MgO in the base glass. Meanwhile, Al_2O_3 was added in proportions of 25, 50, 60 and 75% instead of Li_2O. In some cases, both CaO and Al_2O_3 were introduced together, instead of MgO and Li_2O, respectively, in different proportions. Details of the percentages of the components introduced are given in Table 1.

Glass preparation

The glasses were prepared from purified quartz sand and Reagent grade Li_2CO_3, $CaCO_3$, $MgCO_3$ and calcinide alumina. The batch materials were well mixed in the desired proportions. They were melted in platinum–rhodium crucibles at 1350–1500°C for 4 h, using an electric furnace with SiC heating element. The melts were stirred several times during melting to ensure homogeneity. The samples were cast in the form of

TABLE 1

Chemical composition and thermal expansion coefficient values of the glasses studied

Glass No.	Oxides (mol%)					Expansion coefficients ($°C^{-1} \times 10^{-7}$)	
	Li_2O	CaO	MgO	Al_2O_3	SiO_2	20–300°C	20–500°C
G-1	23.12	–	13.28	–	63.6	78.57	84.50
G-2	23.12	3.32	9.96	–	63.6	81.00	87.20
G-3	23.12	6.64	6.64	–	63.6	83.60	89.68
G-4	23.12	9.96	3.32	–	63.6	85.45	92.70
G-5	23.12	13.28	–	–	63.6	87.50	95.83
G-6	17.34	-	13.28	5.78	63.6	63.10	67.90
G-7	11.56	-	13.28	11.56	63.6	48.21	55.00
G-8	9.25	–	13.28	13.87	63.6	38.21	43.38
G-9	5.78	–	13.28	17.34	63.6	33.00	38.54
G-10	11.56	6.64	6.64	11.56	63.6	55.71	59.05
G-11	9.25	3.32	9.96	13.87	63.6	39.50	45.09
G-12	9.25	13.28	–	13.87	63.6	43.57	49.75

rectangular slabs (1 × 1 cm cross-section and 5–7 cm long), and then they were well annealed to obtain strain-free samples.

Thermal treatment process

For crystallization, a suitable heat-treatment schedule was applied to each glass to obtain glass-ceramic materials of holocrystalline mass with a minimum residual glassy phase without deformation. Therefore, two-step heat-treatment schedules were applied, i.e., the glasses were soaked at 750 or 850°C for 5 h and then at 950 or 1050°C for 3 h, respectively; namely, 1st and 2nd two-step schedules. To study the effect of prolonged heating, a third two-step schedule was applied in which the soaking time of the second temperature step (1050°C) was extended to 15 h.

X-ray analysis

The X-ray diffraction technique was used to identify the nature of the mineral phases formed, using a Siemens X-ray diffractometer type D-500 adopting an Ni filter and Cu radiation. The crystalline phases developed in the glasses by thermal treatment are listed in Table 2.

Thermal expansion measurements

The linear thermal expansion values of glass and crystalline materials were measured using a fused silica dilatometer of Malkin type. Specimens (as rods of 5–7 cm length) were heated at a rate of 10°C min^{-1} and elongation was measured by a graduated dial gauge. Data were obtained for each glass

TABLE 2

Phases developed and thermal expansion coefficient values of the glass-ceramics

Glass No. [a]	Phases developed [b]	Expansion coefficients ($°C^{-1} \times 10^{-7}$)		
		20–300°C	20–500°C	20–900°C
C_1-1	LS_2, C, Q	64.20	73.90	87.02
C_1-2	LS_2, CP, Q	61.20	72.50	85.00
C_1-3	LS_2, D, Q	60.60	71.20	84.30
C_1-4	LS_2, Wss, Q	63.10	74.10	86.70
C_1-5	LS_2, W, Q	68.60	78.10	90.36
C_1-6	S, LS_2, LS, C	28.90	36.80	43.60
C_1-7	S, C	8.19	10.41	14.09
C_2-8	E, S, C	7.14	9.64	12.00
C_3-8	S, C	9.44	11.71	15.03
C_2-9	E, glass (min)	5.95	10.20	15.90
C_3-9	E, S, R, C	4.17	7.71	13.64
C_1-10	S, D	7.60	9.84	13.42
C_2-11	S, E, Cp	6.78	9.37	12.78
C_3-11	S, Cp	8.92	11.45	14.48
C_2-12	S, W, An	9.64	12.50	15.68

[a] C_1 = heated at 750°C for 5 h, 950°C for 3 h; C_2 = heated at 850°C for 5 h, 1050°C for 3 h; C_3 = heated at 850°C for 5 h, 1050°C for 15 h.

[b] LS = lithium metasilicate; LS_2 = lithium disilicate; Q = α-quartz; W = wollastonite; Wss = wollastonite ss; E = B-eucryptite ss; R = cordierite; ss = solid solution; C = clinoenstatite; D = diopside; S = B-spodumene ss; Cp = clinopyroxene ss; An = anorthite; min = minor.

composition from room temperature up to 500°C, while for the glass-ceramic samples, the measurements were extended up to 900°C, using the same heating rate. At least two measurements were made on each specimen and the results were found to be reproducible. The apparatus was calibrated against samples of Corning glass-ceramics (code 9606 and 9608).

The linear coefficient of thermal expansion was then calculated using the equation

$$\alpha = \frac{\Delta L}{L \times \Delta t} + 0.54 \times 10^{-6}$$

where L is the original length of the specimen, ΔL is the increase in length, while Δt is the temperature interval over which the glass is heated. The last term in this equation is the correction factor for the expansion of the quartz tube.

RESULTS

The thermal expansion curves of some of the glasses investigated and their respective crystalline materials are recorded in Figs 1–4. The coefficients of

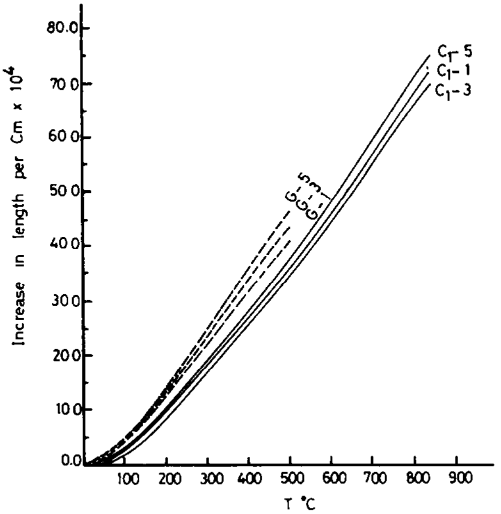

Fig. 1. Linear thermal expansion curves of eutectic and some CaO-containing glasses and their corresponding glass-ceramics. (G) Original glass; (C_1) heated at 750°C for 5 h, 950°C for 3 h.

expansion (α) of the materials studied are given in Tables 1 and 2. Figures 5 and 6 represent the variation of the coefficient of expansion of both glass and crystalline materials as a function of the replacement taking place (i.e., CaO/MgO or Al_2O_3/Li_2O) in the glass composition.

The data obtained from the previously mentioned figures and tables have indicated the following outlines.

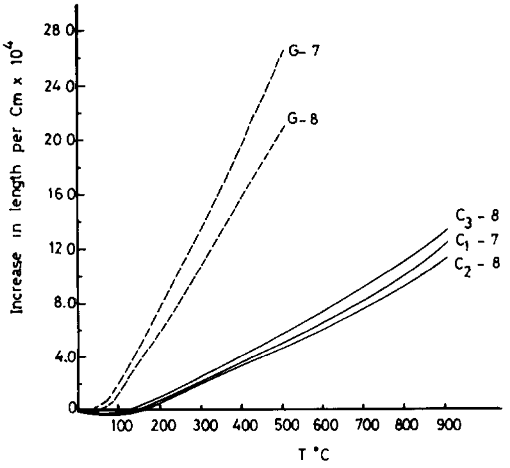

Fig. 2. Linear thermal expansion of some Al_2O_3-containing glasses and their corresponding glass-ceramics (G) Original glass; (C_1) heated at 750°C for 5 h, 950°C for 3 h; (C_2) heated at 850°C for 5 h, 1050°C for 3 h; (C_3) heated at 850°C for 5 h, 1050°C for 15 h.

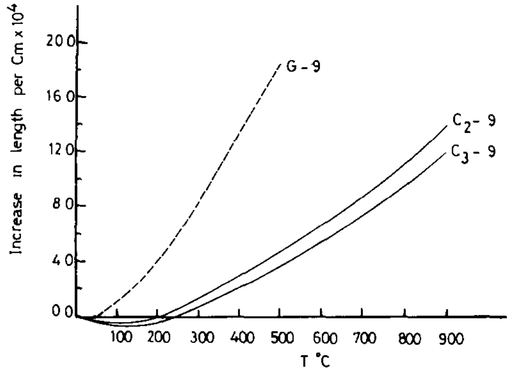

Fig. 3. Linear thermal expansion of glass G-9. (G) Original glass: (C_2) heated at 850°C for 5 h, 1050°C for 3 h; (C_3) heated at 850°C for 5 h, 1050°C for 15 h.

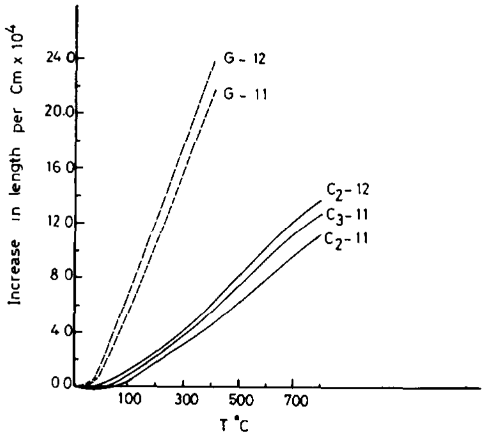

Fig. 4. Linear thermal expansion curves of some CaO and Al_2O_3-containing glasses and their corresponding glass-ceramics. (G) Original glass; (C_2) heated at 850°C for 5 h, 1050°C for 3 h; (C_3) heated at 850°C for 5 h, 1050°C for 15 h.

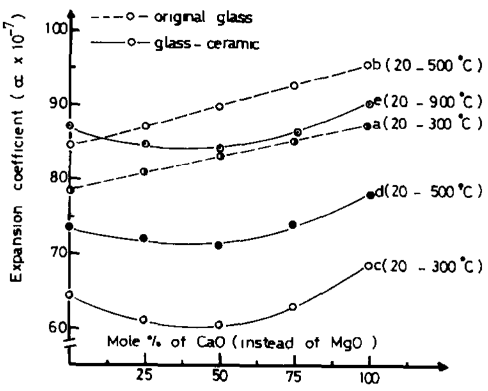

Fig. 5. Change of thermal expansion coefficient of glasses and glass-ceramics as a function of CaO/MgO replacement.

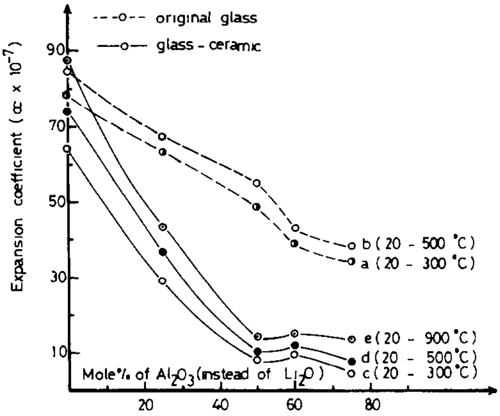

Fig. 6. Change of thermal expansion coefficient of glasses and glass-ceramics as a function of Al_2O_3/Li_2O replacement.

Thermal expansion data of the glasses

The thermal expansion curves (Figs. 1–4) of the investigated glasses are generally similar to those characteristic of most silicate glasses. Most of these expansion curves show a slight curvature.

It is evident that the expansion coefficient (α) of the glasses studied is almost a function of the replacements taking place in the glass composition. Figure 5 clearly indicates that the replacement of MgO by CaO progressively increased the expansion coefficient of the glasses. Table 1 shows that the α-value of the base eutectic (G-1) glass was increased by CaO/MgO replacement and reached a maximum when all the MgO content was replaced by CaO (i.e., G-5).

However, for the Al_2O_3-containing glasses, it is evident that the molecular replacement of Li_2O by Al_2O_3 progressively decreases the expansion coefficient of the glasses. Table 1 indicates that the α-value given by Al_2O_3-containing glasses (G-6–G-9) are much lower than that of glass G-1 (free of Al_2O_3). This is clearly illustrated in Fig. 6 from which it can be seen that the addition of Al_2O_3 to the expense of Li_2O up to an Al_2O_3/Li_2O ratio equal to unity progressively decreases the α-value of the glasses. On further Al_2O_3/Li_2O replacement up to 60% Al_2O_3 substitution, an abrupt decrease is observed. However, at higher Al_2O_3 content a slight decrease in the α-value occurs.

A similar behaviour was recorded for the α-value of the glasses containing both CaO and Al_2O_3. The present results reveal that CaO/MgO replacement in the presence of a constant Al_2O_3 content increases the α-values of the glasses. Meanwhile, their expansion coefficients (α) were greatly decreased by Al_2O_3/Li_2O replacement in the presence of a constant CaO content. Table 1 shows some examples of this behaviour; the α-values given by

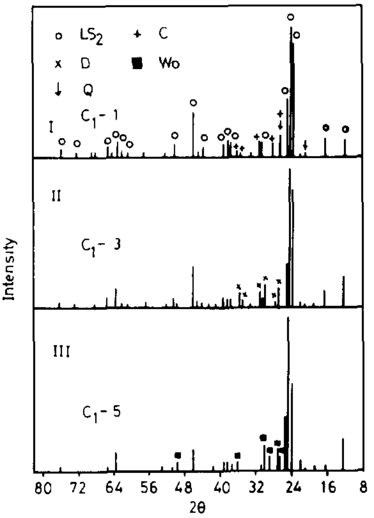

Fig. 7. X-ray diffraction data of eutectic and CaO-containing glasses, crystallized at 750°C for 5 h, 950°C for 3 h.

glasses G-10 and G-11 (with CaO and Al_2O_3) were higher than those of glasses G-7 and G-8 (with Al_2O_3 only), respectively, while the α-values of glasses G-10 and G-12 were much lower than those of glasses G-3 and G-5 (with CaO only).

Phases developed

Investigation of the glass-ceramic materials by X-ray analysis revealed that predominant lithium disilicate ($Li_2Si_2O_5$), clinoenstatite ($MgSiO_3$), and a minority of alpha quartz were crystallized from the eutectic glass (sample C_1-1, Fig. 7-I).

The partial CaO/MgO replacements favoured the formation of some varieties of Ca, Mg-silicate phases. The composition of these varieties was found to depend on the CaO/MgO ratio in the parent glass. At 25% CaO/MgO replacement, clinopyroxene ss.–$MgSiO_3$ + $CaMgSi_2O_6$ was formed. When the CaO/MgO ratio reached unity, diopside–$CaMgSi_2O_6$ was detected (sample C_1-3, Fig. 7-II). At 75% CaO/MgO replacement, the wollastonite ss. phase ($CaSiO_3$–$CaMgSi_2O_6$) was developed. When all the MgO was replaced by CaO, the pure wollastonite phase crystallized out (C_1-5, Fig. 7-III).

The addition of Al_2O_3 to replace Li_2O generally favoured the formation of lithium aluminosilicate phases to the expense of lithium silicate. Clinoenstatite was formed as well, while in some cases cordierite phases were also encountered, especially in a high Al_2O_3-containing sample. The X-ray analysis (Fig. 8) indicated that sample C_1-6 (with 25% Al_2O_3/Li_2O replace-

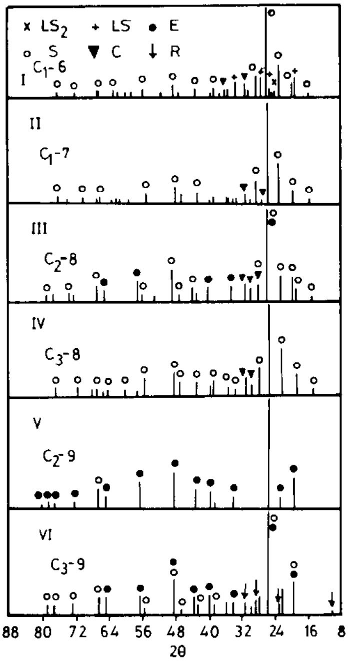

Fig. 8. XRD data for Al_2O_3-containing glasses. (C_1) Heated at 750°C for 5 h, 950°C for 3 h; (C_2) heated at 850°C for 5 h, 1050°C for 3 h; (C_3) heated at 850°C for 5 h, 1050°C for 15 h.

ment) developed B-spodumene ss. as a major constituent with a small amount of lithium metasilicate, lithium disilicate and clinoenstatite. At 50% Al_2O_3/Li_2O replacement, i.e., sample C_1-7, only B-spodumene and clinoenstatite were formed (Fig. 8-II). On further addition of Al_2O_3 up to 60% Al_2O_3/Li_2O replacement (sample C_2-8), B-eucryptite ss. with a small amount of B-spodumene ss. and clinoenstatite were detected by thermal treatment through the 2nd two-step regime, while on prolonged heating (1050°C, 15 h, sample C_3-8), B-spodumene instead of B-eucryptite was formed (Fig. 8-IV). However, at a higher Al_2O_3 content, B-eucryptite ss. was detected in the sample treated by the 2nd two-step regime (i.e., sample C_2-9, Fig. 8-V), while for the long duration treatment (sample C_3-9), B-spodumene ss., B-eucryptite ss., cordierite and traces of clinoenstatite were formed (Fig. 8-VI).

The X-ray analysis of CaO, Al_2O_3-containing samples revealed that sample C_2-10 (with replacement of 50% of both CaO and Al_2O_3) developed B-spodumene ss. and diopside (Fig. 9-I). Investigation of the data of sample C_2-II indicated that B-spodumene, B-eucryptite and clinopyroxene were developed by thermal treatment of the parent glass (G-11) through the 2nd-two-step regime (Fig. 9-II), while for prolonged heating (sample C_3-II, Fig. 9-III), only B-spodumene and clinopyroxene ss. were detected. The X-ray analysis also revealed that sample C_2-12 (with 60% Al_2O_3/Li_2O and

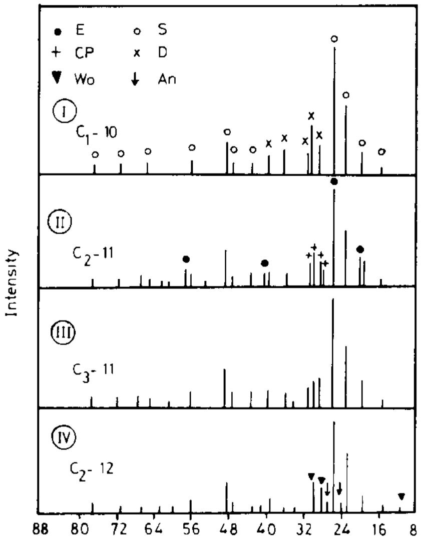

Fig. 9. XRD data for CaO. Al_2O_3-containing glasses. (C_1) Heated at 750°C for 5 h, 950°C for 3 h; (C_2) heated at 850°C for 5 h, 1050°C for 3 h; (C_3) heated at 850°C for 5 h, 1050°C for 15 h.

100% CaO/MgO replacement) developed B-spodumene, wollastonite and anorthite (Fig. 9-IV).

Thermal expansion of the corresponding glass-ceramics

The data obtained revealed that the expansion coefficients of the crystalline products were generally much lower than those of the corresponding glasses.

The partial replacement of MgO by CaO in the base glass up to a CaO/MgO ratio of unity generally decreased the α-value of the crystalline materials. However, at higher CaO/MgO replacement, the expansion coefficient was increased. The composition dependence of the expansion coefficient relationship (Fig. 5) showed that the α-value exhibited a minimum value for glass-ceramics containing 50% CaO/MgO substitution, after which it increased with a gradual increase in the CaO content and reached a maximum value when all the MgO was replaced by CaO.

The addition of Al_2O_3 instead of Li_2O greatly decreases the expansion coefficient of the crystalline materials. Figure 6 clearly shows that the gradual replacement of Li_2O by Al_2O_3 up to 50% Al_2O_3/Li_2O ratio progressively decreases the α-values of the crystalline material. At high Al_2O_3/Li_2O replacement, some fluctuation in the α-values was observed.

With respect to the mixed effect of CaO and Al_2O_3 on the expansion coefficient of the crystalline materials, it is seen that the α-value of the material is greatly dependent on the CaO/MgO and/or Al_2O_3/Li_2O ratio present in the glass composition. CaO/MgO replacement may decrease or increase the α-values of Al_2O_3-containing materials, while Al_2O_3/Li_2O replacement greatly lowers the α-values of the CaO-containing material. Table 2 indicates that the α-values of samples C_1-10 and C_3-11 (with CaO and Al_2O_3) were slightly lower than those of samples C_1-7 and C_3-8 (with Al_2O_3), respectively. Also, the α-value of sample C_2-11 (with low CaO and high Al_2O_3 content) was lower than that of sample C_2-12 (with high CaO and Al_2O_3 content). However, the expansion coefficients of samples C_1-10 and C_2-12 were much lower than those of samples C_1-3 and C_1-5 (with CaO only), respectively.

The effect of prolonged heating

The α-values of the thermally crystallized glasses were influenced by the duration of the heat treatment applied. Table 2 and Figs. 2–4 indicate that the α-value of sample C_3-8 (of long duration) was higher than that of sample C_2-8 (of short duration), while the α-value of sample C_3-9 (of long duration) was lower than that of sample C_2-9 (of short duration). The same observation was also made in the case of CaO, Al_2O_3-containing samples (e.g., C_2-11 and C_3-11).

DISCUSSION

Generally, the volume of a material increases with increasing temperature because of the increasing amplitude of vibration of atoms, associated with changing interatomic distances and bond angles [6]. From lattice energy considerations, the ionic vibrations are anharmonic and, as a result of increasing amplitude of vibration, the interionic distance increases [7]. This mechanism alone is responsible for the flat straight line observed in the expansion curves of the glasses. In the most common glasses, the atomic distribution function changes continuously, especially at sufficiently high temperatures, and contributes to a major portion of the observed expansion.

The thermal expansion of glass is not only a function of temperature, but also depends, among other factors, on the glass composition.

The thermal expansion may be related to the internal structure and to the number and size of the ionic aggregates [8]. The nature of the particular cations should be also taken into consideration. The bond strength and character were suggested to govern the thermal expansion [9]. The open, less rigid or loosely compact nature of the structure favours the increase in thermal expansion. Also, the replacement of a cation with another of higher bond strength will decrease the thermal expansion coefficient. The binding energy increases with increasing valency and decreasing size of the atom [10,11]. The thermal expansion is also assumed to increase with increasing ionic character of the bonding.

In the case of properties which are highly sensitive to structural cohesiveness, the smaller cations with higher field strengths seem to produce more strongly bound structures than the larger cations, and the smaller cation glasses are generally characterized by larger moduli and smaller expansion coefficients [12]. Also, the possibility arises that some of the divalent metal cations, like Mg^{2+} and Zn^{2+}, can participate in the glass structure and form network tetrahedra units. The vibration of these groups is not so easy as if the cations are in interstitial positions and, hence, a decrease is observed in the expansion coefficients of a glass containing either of these cations.

These criteria may interpret the increase in thermal expansion coefficient of the glasses to be due to the replacement of a cation by another of larger size (lower field strength).

To realize that the addition of CaO to replace MgO of the present alkali silicate glasses increases the thermal expansion coefficient, we may suggest that the Ca^{2+} ions in such silicate glasses exhibit the octahedral coordination state with oxygen [13]. These octahedral calcium groups posses a lower single-bond strength (32 kcal mol^{-1}) compared with that of Mg^{2+} in a tetrahedral coordination (37 kcal mol^{-1}). Therefore, the thermal expansion coefficient of the glasses is then increased.

In Al_2O_3-containing glasses, the role of Al^{3+} (ionic size 0.50 Å, single-bond strength with oxygen of about 79 kcal mol^{-1}) replacing Li^{1+} (ionic size 0.6 Å, single-bond strength with oxygen of 36 kcal mol^{-1}) is quite different. The ability of aluminium as an intermediate oxide to form the AlO_4 group, or to be housed in octahedral coordination in the glass interstices is known. Our results indicate that Al^{3+} preferably exhibits a tetrahedral coordination in the present glass which explains the decrease in the expansion coefficient on addition of Al_2O_3 to replace Li_2O in the glasses.

With the first addition of Al_2O_3 up to an Al_2O_3/Li_2O ratio of unity, the aluminium coordination is expected to change from three to four by the additional oxygen with the lithium occupying interstitial positions. This change is associated with a change in bonding character from 2- to 3-dimensional with an attendant increase in the tightness of the structure initiating a progressive decrease in the expansion coefficient of the glass. With a further increase in Al_2O_3 content ($Al_2O_3/Li_2O > 1$), the possibility of a decrease is non-bridging oxygen would result. At high Al_2O_3 concentration the number of non-bridging oxygen ions is too small to disturb the coherence of the network to a measurable degree. The combined effect of decreasing the number of non-bridging oxygen ions and the possible increase of the aluminium in tetrahedral coordination might explain the abrupt and progressive decrease in the thermal expansion coefficient with high Al_2O_3 content in the glasses.

The same explanation can hold in the case of the data obtained for glasses containing both CaO and Al_2O_3.

The thermal expansion coefficient of glass-ceramics can be markedly different from that of the glasses. Thermal treatment of the glasses generally introduces crystalline phases having expansion coefficients usually different from that of the parent glass. Therefore, the glass-ceramic materials may have a high or low coefficient of expansion depending on the crystal phases formed and the residual glass matrix [5]. In most cases, the expansion coefficient of the crystalline materials generally increases with increasing glass phase content in the material [14]. However, in certain cases, the changes in composition of the residual glass phase result in changes of the thermal expansion of a sufficient magnitude to counterbalance the effect of the development of the crystal phase. Consequently, the glass-ceramic and the parent glass have closely similar thermal expansion coefficients.

The glass-ceramic is a composite material and its thermal expansion coefficient is a function of the thermal expansion coefficients and elastic properties of all phases present, including the residual glass. Thus, while the development of crystal phases usually causes major changes in the expansion coefficient, crystallization will alter the composition of the residual glass phases from that of the parent glass; this must be taken into account when attempting to analyze the thermal expansion of glass-ceramics in relation to their constitution.

Crystallization of glasses of the Li_2O–Al_2O_3–SiO_2 system yields products of much lower coefficients of expansion than those of the original glass. Both B-eucryptite and the composition corresponding to Li_2O–Al_2O_3–$3SiO_2$ have negative coefficients of expansion [15,16]. The B-eucryptite gives a high negative expansion of -86×10^{-7} °C^{-1} in the range 20–700°C [5].

The expansion coefficient of B-spodumene and its solid solution have low positive values from 3×10^{-7} to 9×10^{-7} °C^{-1}, in accordance with the relative proportion of spodumene, quartz or cristobalite phases. Stuffed derivatives of high quartz structures show positive, low coefficients of expansion [5]. In Li–Mg and Zn–aluminosilicates, Li, Zn-containing high quartz phases exhibit negative or slightly positive expansion coefficients. The incorporation of Mg increases the thermal expansion [17].

Cordierite also has a relatively low positive thermal expansion coefficient (26×10^{-7}, 20–700°C) [18]. The pyroxenes, wollastonite, anorthite and lithium silicate phases, on the other hand, have high, positive values of thermal expansion. Diopside has values of $50–150 \times 10^{-7}$ °C^{-1} (20–600°C) [19]. The aggregate linear thermal expansion coefficients of enstatite and clinoenstatite between 300–700°C are, respectively, 120×10^{-7} and 135×10^{-7} [20]. Anorthite and wollastonite have thermal expansion coefficient values of 66×10^{-7} (100–900°C) and 94×10^{-7} (100–200°C) [18,21], respectively, while lithium disilicate has a value of 110×10^{-7} (20–600°C).

Therefore, the effect of a particular phase is, of course, dependent on its concentration in the glass-ceramic as well as on its individual thermal expansion characteristics with the result that glass-ceramics containing the same crystalline phase, but in different proportions, may have noticeably different thermal expansion coefficients.

The present results revealed that the replacement of MgO by CaO in the glass up to 50% MgO substitution decreased the α-values of the corresponding glass ceramics. This may be attributed to the formation of the relatively lower expanding diopside phase instead of the higher expanding clinoenstatite phase which has been formed in the CaO-free sample (eutectic C-1). However, by further CaO/MgO replacement, the thermal expansion coefficient of the material was increased. This may be attributed to the formation of the wollastonite phase.

In Al_2O_3-containing samples, the replacement of Li_2O by Al_2O_3 in the glass up to an Al_2O_3/Li_2O molar ratio equal to unity, progressively decreased, to a great extent, the α-values of the corresponding crystalline samples. This may be due to the formation of the very low, positive thermally expanding B-spodumene solid solution as the dominant phase which has been formed at the expense of the higher thermally expanding lithium disilicate. However, on further Al_2O_3/Li_2O replacement up to 60% Al_2O_3 replacement, the expansion coefficient of the holocrystalline materials (i.e., C_3-8) was slightly increased.

The contribution of a particular crystal phase to the thermal expansion of a glass-ceramic may be modified if the crystal enters into solid solution with another phase. A more significant fact is that Mg^{2+} and Al^{3+} in pseudo-octahedral stuffing positions cause an increase in the thermal expansion of B-quartz ss. glass-ceramics [17,22]. Both samples C_1-7 and C_3-8 are composed of B-spodumene ss. and clinoenstatite; however, sample C_1-7 contains just enough Al_2O_3 for Li_2O to form B-spodumene, while sample C_3-8 contains Al_2O_3/Li_2O at a ratio greater than unity (i.e., greater than the requirement for B-spodumene formation). Therefore, the excess of Al_2O_3 present in the latter sample was incorporated together with a proper amount of Mg^{2+} in B-spodumene ss. Accordingly, based on the nature of the solid solution described above, the considerable difference between the thermal expansion of samples C_1-7 and C_3-8 is most probably due to the incorporation of $Mg(AlO_2)_2$ in the B-spodumene structure formed in sample C_3-8.

At higher Al_2O_3/Li_2O replacement (i.e., 75% Al_2O_3 replacement) the expansion coefficient of holocrystalline materials (i.e., C_3-9) again decreased. This may be attributed to the formation of the B-eucryptite ss. phase among the crystallization products of such a sample.

Prolonged heating greatly affected the thermal expansion of Al_2O_3-containing samples, the α-values of sample C_3-8 (of long duration), were higher than that of sample C_2-8 (of short duration). Actually, the thermal treatment of the latter sample at 1050°C for 3 h developed B-eucryptite ss., B-spodumene ss. and clinoenstatite; however, for prolonged heating (15 h), the

B-eucryptite ss. phase had mostly been converted into B-spodumene ss. in sample C_3-8 resulting in a slight increase in the thermal expansion of the material (Table 2).

Also, the higher α-values shown by sample C_2-9 as compared with that of sample C_3-9 may be attributed to the fact that sample C_3-9 is composed of low-expanding B-eucryptite ss., B-spodumene ss. and cordierite phases, while sample C_2-9 contains B-eucryptite ss. together with the remaining glassy phase. This glassy phase may cause an increase in the thermal expansion of the material.

In CaO, Al_2O_3-containing glasses, it was observed that the presence of CaO and Al_2O_3 together almost decreased the thermal expansion of the crystalline samples. Al_2O_3 was most effective in this sense. The α-values of samples C_1-10 and C_3-11 (with CaO and Al_2O_3) were slightly lower than those of samples C_1-7 and C_3-8 (with Al_2O_3), respectively. This may be attributed to the formation of the pyroxene molecules (diopside) in the former sample instead of clinoenstatite which were formed in the latter samples.

Also, the data obtained for sample C_2-12 (with high CaO and Al_2O_3) were greater than those for sample C_2-11 (with low CaO/MgO and Al_2O_3). This may be attributed to the formation of the high-expanding wollastonite and anorthite phases instead of clinopyroxene ss. formed in sample C_2-11.

The formation of the very low-expanding B-spodumene ss. phase in samples C_1-10 and C-12 (with CaO, Al_2O_3) may explain the lower values as compared with those obtained from the corresponding samples C_1-3 and C_1-5 in which the high-expanding lithium disilicate was formed.

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