

THERMAL EXPANSION PROPERTIES OF SOME VITREOUS AND CRYSTALLINE SILICATE MATERIALS

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ABSTRACT

The thermal expansion coefficient (α) of some multi-component silicate glasses with special reference to their respective crystalline products have been measured using an ORTON automatic recording dilatometer. The glass compositions are of the $\text{Li}_2\text{O}(\text{Al}_2\text{O}_3)\text{-MgO}(\text{CaO}, \text{ZnO})\text{-SiO}_2$ type where MgO may be replaced by CaO or ZnO, and Al_2O_3 may replace Li_2O .

The expansion coefficients of the glasses increased on replacement with ZnO or CaO/MgO. However, the α -values of the glasses markedly decreased on $\text{Al}_2\text{O}_3/\text{Li}_2\text{O}$ replacement. The change in the expansion coefficient of the glasses is discussed in relation to factors such as polarization, field strength and the ionic radii of the incorporated cations, and their effects on the geometrical arrangement of the building units of the glassy network.

The expansion coefficients changed markedly on conversion of the glasses into glass-ceramic materials. In such cases the data obtained were correlated to the nature, composition and concentration of all phases formed in the materials.

INTRODUCTION

The changes in dimension of materials which occur with a change in temperature are of great importance from a number of points of view. 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 changes in the distribution of forces with increasing thermal vibration [1].

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. If a material of high thermal shock resistance is required, the coefficient of thermal expansion should be as low as possible in order to minimize strain resulting from temperature gradients within the material. The thermal expansion of a vitreous material is primarily related to its composition, thermal history and internal structure, because of its sensitivity to the number and size of the building unit

aggregates [2]. 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 [3].

The thermal expansion coefficient of crystalline materials such as glass-ceramics is generally quite different from that of their respective parent glasses [4]. 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 [4]. The degree of thermal expansion was found to be dependent on the nature of the associated crystalline phases and on the content of glassy phase present in the material.

EXPERIMENTAL

The effect of ZnO/MgO, CaO/MgO and/or Al₂O₃/Li₂O replacements on the thermal expansion coefficients (α -values) of the crystalline-glass materials based on the multi-component Li₂O(Al₂O₃)-MgO(CaO,ZnO)-SiO₂ system has been investigated. ZnO or CaO was added in various proportions such as 25%, 50% and 75% in replacement of the MgO content. Meanwhile, Al₂O₃ was introduced in proportions of 25% and 50% in replacement of Li₂O. In some cases both ZnO and CaO were introduced together with Al₂O₃ in different proportions in replacement of MgO and Li₂O respectively. Details of the percentages of the components introduced are given in Table 1.

TABLE 1

Chemical composition and thermal expansion coefficient values for the glasses studied

Glass No.	Oxide content (mol%)						Expansion coefficient α at 500 °C ($^{\circ}\text{C}^{-1} \times 10^{-7}$)
	Li ₂ O	CaO	MgO	ZnO	SiO ₂	Al ₂ O ₃	
G ₁	23.12	—	13.28	—	63.6	—	84.53
G ₂	23.12	—	9.96	3.32	63.6	—	85.8
G ₃	23.12	—	6.64	6.64	63.6	—	87.2
G ₄	23.12	—	3.32	9.96	63.6	—	88.3
G ₅	23.12	3.32	6.64	3.32	63.6	—	88.54
G ₆	23.12	6.64	3.32	3.32	63.6	—	91.00
G ₇	23.12	9.94	—	3.32	63.6	—	93.40
G ₈	17.34	3.32	6.64	3.32	63.6	5.78	68.20
G ₉	11.56	3.32	6.64	3.32	63.6	11.56	49.70
G ₁₀	11.56	6.64	3.32	3.32	63.6	11.56	52.27
G ₁₁	11.56	9.96	—	3.32	63.6	11.56	54.35

Material preparation

The glasses were prepared from purified quartz sand and reagent grade Li_2CO_3 , CaCO_3 , MgCO_3 , ZnO , and calcined alumina. After thorough mixing the batches were melted in Pt-2%Rh crucibles at 1300–1400 °C for 4 h, with occasional stirring to ensure complete homogeneity, using an electric furnace with an SiC heating element. The samples were cast in the form of rectangular slabs (cross section 1×1 cm and length 2.49–2.52 cm). They were then well annealed to minimize the strain.

Suitable heat-treatment schedules were applied in order to obtain glass-ceramic materials of holocrystalline mass having minimum residual glassy phase without deformation. This was done by applying two-step heat-treatment schedules, i.e. the glasses were soaked at 520 °C or 630 °C for 2 h and then at 830 °C or 900 °C for 5 h respectively.

A Siemens X-ray diffractometer type D-500 with an Ni filter and using Cu radiation was used to identify the crystalline phases developed in the glass samples.

Thermal expansion measurements

The coefficient of thermal expansion of the samples tested was measured using an ORTON automatic recording dilatometer with a heating rate of 6°C min^{-1} and an expansion multiplier of 0.2. This dilatometer employs program correction to room temperature and according to type of holder tube used. Data were obtained for the parent glass specimens from room temperature up to 500 °C, while for the corresponding crystalline specimens the measurements were extended up to 850 °C. Linear thermal expansion coefficients were calculated using the general equation

$$\alpha = (\Delta L/L \Delta t) \times 10^{-7} \quad (1)$$

where L is the original length of the specimen, ΔL is the increase in length and Δt is the temperature interval over which the sample is heated.

RESULTS

The coefficients of expansion α of the samples tested in the glass and the crystalline state are given in Tables 1 and 2 respectively. The thermal expansion curves of the crystalline samples are shown in Fig. 1. Figures 2–5 below report the variation in the coefficient of expansion of both glassy and crystalline materials as a function of the replacements taking place (i.e. ZnO/MgO , CaO/MgO and/or $\text{Al}_2\text{O}_3/\text{Li}_2\text{O}$) in the glass composition. The data reveal the following trends.

TABLE 2

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

Glass No.	Phases developed ^a	Expansion coefficient α ($^{\circ}\text{C}^{-1} \times 10^{-7}$)			
		300 $^{\circ}\text{C}$	500 $^{\circ}\text{C}$	700 $^{\circ}\text{C}$	800 $^{\circ}\text{C}$
C ₁	LS ₂ , C, QZ (minor)	62.58	81.03	90.35	95.113
C ₂	LS ₂ , LZnS, α -QZ, C	65.8	85.6	94.6	98.700
C ₃	LS ₂ , α -QZ, LZnS, C (decreased)	70.5	90.0	99.8	105.000
C ₄	LS ₂ , α -QZ, Li ₂ Zn(Mg)SiO ₄	74.8	95.68	106	112.000
C ₅	LS ₂ , QZ(α , β), LZnS, Cp(ss)	62.83	78.18	84	86.810
C ₆	LS ₂ , QZ(α , β), LZnS, Wo, Di	56	69.4	77.33	79.970
C ₇	LS ₂ , QZ(α , β), LZnS, L ₂ C ₃ S ₆	57.6	71	76.5	81.000
C ₈	β -sp(ss), LS ₂ , LZnS, Cp(ss)	28.22	40.27	47.58	50.570
C ₉	β -sp(ss), LZnS, Cp(ss)	23.24	34.86	40.12	42.850
C ₁₀	β -sp(ss), β -euc(ss), Di, Zn-mel	18.8	31.1	37.1	40.200
C ₁₁	β -sp(ss), Zn-mel, Wo	16.53	28.5	35.95	38.440

^a LS₂, Lithium disilicate; C, clinoenstatite; QZ, quartz; LZnS, lithium zinc orthosilicate; Cp, clinopyroxene; ss, solid solution; Wo, wollastonite; Di, diopside; L₂C₃S₆, lithium calcium silicate; β -sp, β -spodumene; β -euc, β -eucryptite; Zn-mel, Ca₂ZnSi₂O₇.

Thermal expansion data of the glasses

Figures 2 and 3 clearly show that both ZnO/MgO and CaO/MgO replacements progressively increase the expansion coefficient of the glass. Table 1 shows that the α -value of the Li₂O-MgO-SiO₂ base glass (G₁) increases on ZnO/MgO replacement (G₂, G₃ and G₄). A similar behaviour was observed for the α -values of those glasses where various CaO/MgO replacements had been made whilst maintaining a constant ZnO (G₂, G₅, G₆ and G₇) or Al₂O₃ (G₉, G₁₀ and G₁₁) content. However, for those glasses containing various proportions of Al₂O₃, it is evident that the expansion coefficients of the glasses progressively decrease on Al₂O₃/Li₂O replace-

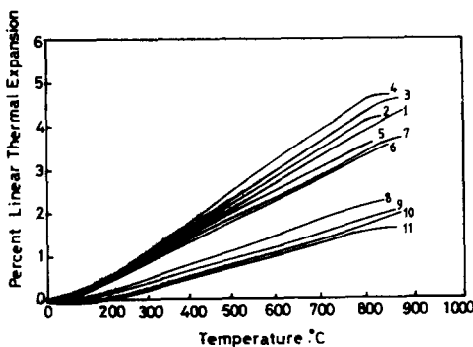


Fig. 1. Linear thermal expansion curves of the glass-ceramics.

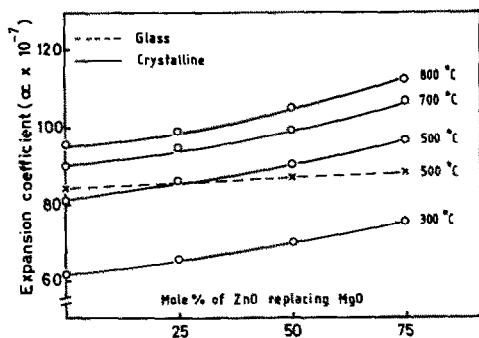


Fig. 2. Change in expansion coefficient of glasses and glass-ceramics as a function of ZnO/MgO replacement.

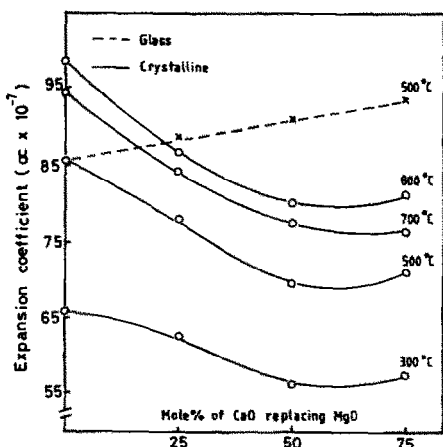


Fig. 3. Change in expansion coefficient of glasses and glass-ceramics as a function of CaO/MgO replacement.

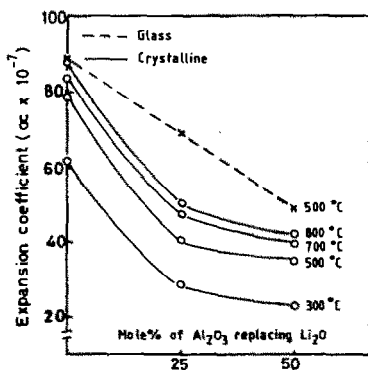


Fig. 4. Changes in expansion coefficient of glasses and glass-ceramics as a function of Al₂O₃/Li₂O replacement.

ment (Fig. 4). Table 1 clearly shows that the addition of Al_2O_3 instead of Li_2O decreases the α -value of the glasses (G_5 , G_8 and G_9).

Thermal expansion of the crystalline samples (glass-ceramics)

The data obtained reveal that the expansion coefficients α of the crystalline specimens (at 500°C) were in most cases lower than those of the corresponding glasses. The addition of ZnO (in place of MgO) in the base glass generally increased the α -value of the crystalline products. The composition dependence of the expansion coefficient (Fig. 2) shows a progressive increase in the α -values of the crystalline material on ZnO/MgO replacement. The partial replacement of MgO by CaO up to a CaO/MgO ratio of unity generally decreases the α -value of the material. However, at higher degrees of CaO/MgO replacement, the expansion coefficient increases slightly. The change in thermal coefficient as a function of the CaO/MgO ratio in the glass (Fig. 3) shows that the α -value exhibits a minimum value for crystalline material at 50% CaO/MgO replacement, after which, it increases with increasing CaO content.

A large decrease in the α -value of the material was observed on addition of Al_2O_3 instead of Li_2O . Figure 4 clearly shows that the partial replacement of Li_2O by Al_2O_3 greatly decreases the expansion coefficient of the crystalline materials. With respect to the addition of mixed CaO and Al_2O_3 , a slight decrease in the α -value was observed on CaO/MgO replacement of up to 75% with a constant Al_2O_3 content (Fig. 5).

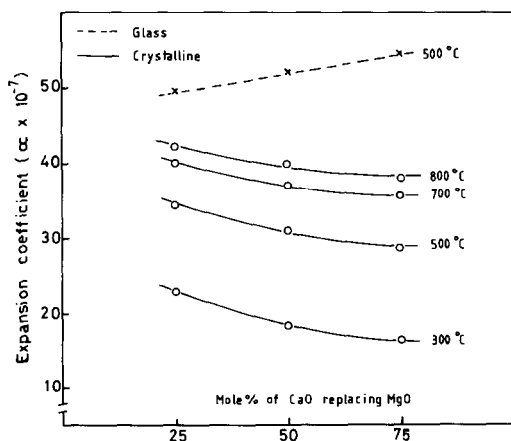


Fig. 5. Change in expansion coefficient of glasses and glass-ceramics as a function of CaO/MgO replacement at constant Al_2O_3 .

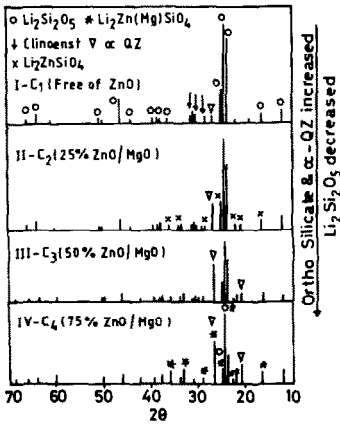


Fig. 6. X-ray data for base glasses and ZnO-containing glasses crystallized at 520°C/2 h–830°C/5 h.

Crystalline phases developed

Predominantly lithium disilicate ($\text{Li}_2\text{Si}_2\text{O}_5$), clinoenstatite (MgSiO_3) and a small amount of α -quartz were identified using X-ray analysis of samples of the Li_2O – MgO – SiO_2 base glass (C_1 , Fig. 6). However, on addition of ZnO (instead of MgO) up to ZnO/MgO ratios of unity, $\text{Li}_2\text{ZnSiO}_4$ and α -quartz were formed together with $\text{Li}_2\text{Si}_2\text{O}_5$ and clinoenstatite (C_2 and C_3 , Fig. 6). At higher degrees of ZnO/MgO replacement (i.e. 75%), $\text{Li}_2\text{Zn}(\text{Mg})\text{SiO}_4$ together with α -quartz and $\text{Li}_2\text{Si}_2\text{O}_5$ were formed [5] (C_4 , Fig. 6). X-ray analysis (Fig. 6) indicated that both lithium zinc silicate and α -quartz were formed at the expense of the $\text{Li}_2\text{Si}_2\text{O}_5$ phase.

For crystalline materials of various CaO/MgO ratios (at constant ZnO content), a series of Ca,Mg-silicate phases were also developed [6]. These include the formation of such varieties as clinopyroxene(ss) (MgSiO_3 – $\text{CaMgSi}_2\text{O}_6$) at 25% CaO/MgO replacement (C_5 , Fig. 7), diopside– $\text{CaMgSi}_2\text{O}_6$ at 50% CaO/MgO replacement (C_6 , Fig. 7) and wollastonite– CaSiO_3 at 75% CaO/MgO replacement. In some cases, at high degrees of CaO/MgO replacement, lithium calcium silicate– $\text{Li}_2\text{Ca}_3\text{Si}_6\text{O}_{16}$ was crystallized from the glass at temperatures as high as 850°C (C_7 , Fig. 7).

The addition of Al_2O_3 in replacement of Li_2O (C_8 and C_9) led to the formation of a lithium aluminosilicate solid solution (β -eucryptite and/or β -spodumene(ss)) at the expense of $\text{Li}_2\text{Si}_2\text{O}_5$ [7]. The β -eucryptite was generally favoured at lower temperatures, however; at higher temperatures (850°C), β -spodumene was formed instead. At 25% $\text{Al}_2\text{O}_3/\text{Li}_2\text{O}$, $\text{Li}_2\text{Si}_2\text{O}_5$, $\text{Li}_2\text{ZnSiO}_4$ and clinopyroxene were formed together with β -spodumene (C_8 , Fig. 8), while at higher degrees of $\text{Al}_2\text{O}_3/\text{Li}_2\text{O}$ replacement (i.e. 50%) β -spodumene, $\text{Li}_2\text{ZnSiO}_4$ and diopside were detected (C_9 , Fig. 8). For samples having various CaO/MgO ratios (at constant ZnO and Al_2O_3

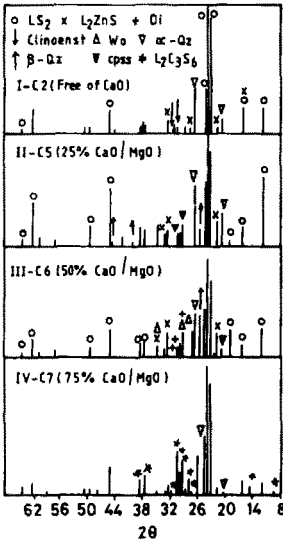


Fig. 7. X-ray data for CaO,ZnO-containing glasses (with constant ZnO and various CaO contents) crystallized at 520 °C/2 h–830 °C/5 h.

contents), clinopyroxene(ss), $\text{Li}_2\text{ZnSiO}_4$ and β -spodumene(ss) were formed at 25% CaO/MgO replacement (C_9). Diopside, hardystonite ($\text{Ca}_2\text{ZnSi}_2\text{O}_7$) and β -spodumene were identified at 50% CaO/MgO replacement (C_{10}); however, wollastonite was formed instead of diopside at higher degrees of CaO/MgO replacement (C_{11}).

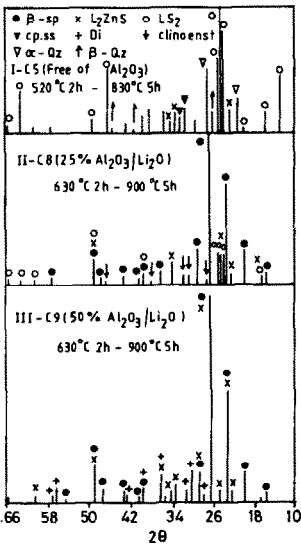


Fig. 8. X-ray data for CaO,ZnO, Al_2O_3 -containing glasses (constant CaO and ZnO and various Al_2O_3 contents).

DISCUSSION

In general, the increase in volume of a material with an increase in temperature would result owing to the increase in amplitude of vibration of atoms associated with changing interatomic distances and bond angles [8]. 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 [9]. The nature of the particular cations and their bonding to each other should be also taken into consideration.

Weyl and Marboe [1] attributed the increase in thermal expansion of well annealed glasses in their softening range to the formation of defects such as vacant anion sites or incomplete coordination. Defects introduce asymmetries into the thermal vibration. The open, less rigid or loosely compact nature of the structure favours an increase in thermal expansion. Also, the replacement of one 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]. 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 cohesivity, smaller cations having a higher field strength seem to produce more strongly bound structures than larger cations, and smaller-cation glasses are generally characterized by large module and smaller expansion coefficients [12]. Also, the possibility arises that some of the divalent metal cations, such as Mg^{2+} and Zn^{2+} , can participate in the glass structure and form networks of tetrahedral units. The mechanism of vibration of these groups is not as simple 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. The increase in the thermal expansion coefficient of the glass may thus be explained as being a result of the replacement of one cation by another of larger size (lower field strength). Both Ca^{2+} and Zn^{2+} ions have a lower field strength and a lower single bond strength compared with those of Mg^{2+} ions [13]. The expansion coefficients of the glasses under discussion are therefore expected to increase with addition of either CaO or ZnO instead of MgO.

The effect of Al_2O_3/Li_2O replacement is quite different. Both Al^{3+} and Li^+ have oxygen single-bond strengths of 79 and 36 kcal mol⁻¹ respectively. The ability of aluminium to form AlO_4 or AlO_6 groups in the glass structure is known. Our results indicate that Al^{3+} preferably has a tetrahedral coordination in the glass under discussion, which explains the decrease in the expansion coefficient on Al_2O_3/Li_2O replacement. With addition of

TABLE 3

Literature data for the thermal expansion coefficients α of some common crystalline phases formed in glass-ceramics

Phases	Expansion coefficient α ($^{\circ}\text{C}^{-1} \times 10^{-7}$)		References	
Quartz SiO_2	237	(20–600 $^{\circ}\text{C}$)	4	
Enstatite MgSiO_3	120	(300–700 $^{\circ}\text{C}$)	15	
Clinoenstatite MgSiO_3	{	78	(100–200 $^{\circ}\text{C}$)	15
		135	(300–700 $^{\circ}\text{C}$)	15
Diopside $\text{CaMgSi}_2\text{O}_6$	50–150	(20–600 $^{\circ}\text{C}$)	16	
Wollastonite CaSiO_3	94	(100–200 $^{\circ}\text{C}$)	17	
Lithium disilicate $\text{Li}_2\text{Si}_2\text{O}_5$	110	(20–600 $^{\circ}\text{C}$)	4	
Lithium zinc orthosilicate $\text{Li}_2\text{ZnSiO}_4$	140	(200–700 $^{\circ}\text{C}$)	18	
β -eucryptite	{	–86	(20–700 $^{\circ}\text{C}$)	4, 19
		–64	(20–100 $^{\circ}\text{C}$)	
β -spodumene(ss)	3–9	(20–100 $^{\circ}\text{C}$)	4	

Al_2O_3 , the Al^{3+} coordination is expected to change from 3 to 4 because of 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.

Unlike glasses, the expansion coefficient of the crystalline materials is quite different. It may increase, decrease, or remain virtually unchanged during the crystallization process, depending on the type and quantity of the crystalline mineral phases formed during this process. The thermal expansion coefficient of a glass-ceramic material is usually a function of the expansion coefficient and of the elastic properties of all phases present, including residual glass [4]. In most cases, the expansion coefficient of this material generally increases with increasing glass phase content [14]. Thus, while the development of crystal phases usually causes major changes in the expansion coefficient, crystallization will alter the composition of the residual glass phase from that of the parent glass, which must be taken into account when attempting to analyse the thermal expansion coefficient of glass-ceramics in relation to their composition.

Literature data for the thermal expansion coefficients of some common crystal phases formed in glass-ceramics are listed in Table 3. They indicate that the pyroxenes (enstatite, clinoenstatite and diopside), wollastonite, lithium disilicate, lithium zinc silicate and quartz have high positive expansion coefficients. Meanwhile, crystal phases based on the $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system have much lower thermal expansion coefficients. β -eucryptite and the composition corresponding to $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-3\text{SiO}_2$ have negative coefficients of expansion [19]. β -spodumene and its solid solutions (with silica) have low positive α -values depending upon the SiO_2 content accommodated

in the spodumene structure. In Li–Mg and Zn–aluminosilicate, Li,Zn-containing high quartz phases exhibit negative or slightly positive expansion coefficients. The incorporation of Mg increases the α -values [20].

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. This has the result that glass–ceramics containing the same crystalline phase but in different proportions may have noticeably different thermal expansion coefficients.

The results discussed here reveal that ZnO/MgO replacement in the glasses progressively increases the α -values of the corresponding glass–ceramics, which may be attributed to the formation of the high-expansion $\text{Li}_2\text{ZnSiO}_4$ and quartz instead of the relatively low-expansion $\text{Li}_2\text{Si}_2\text{O}_5$ phase.

However, on CaO/MgO replacement up to 50% substitution, the α -value of the crystalline material decreases. This may be due to the formation of the relatively low-expansion diopside phase instead of the higher-expansion clinoenstatite phase. At a higher CaO/MgO ratio, the α -value increases slightly, which may be related to the formation of an $\text{Li}_2\text{Ca}_3\text{Si}_6\text{O}_{16}$ phase.

In Al_2O_3 -containing samples, the replacement of Li_2O by Al_2O_3 in the glass up to an $\text{Al}_2\text{O}_3/\text{Li}_2\text{O}$ molar ratio equal to unity, progressively decreased the α -values of the corresponding crystalline samples to a large extent. This may be a result of the formation of the very low, positive, thermally expanding β -spodumene solid solution as the dominant phase which has been formed at the expense of the higher thermally expanding lithium disilicate.

A slight decrease in the α -values was obtained for glass–ceramics of various CaO/MgO ratios at a constant Al_2O_3 content (C_9 – C_{11} , Fig. 5 and Table 2). This may be related to the formation of diopside and Zn-melilite ($\text{Ca}_2\text{ZnSi}_2\text{O}_7$) in samples 10 and 11 having high CaO/MgO ratio, instead of clinopyroxene(ss) and $\text{Li}_2\text{ZnSiO}_4$ formed in sample 9.

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