Thermochimica Acta, 191 (1991) 187–199
Elsevier Science Publishers B.V., Amsterdam

Contribution of manganese oxide to the thermal expansion of some silicate glasses and their crystalline solids

Samia N. Salama and S.M. Salman

Glass Research Dept., National Research Centre, Dokki, Cairo (Egypt)

(Received 29 March 1991)

Abstract

The thermal expansion characteristics of some lithium silicate materials containing various MnO/CaO and MnO/MgO ratios together, in some cases, with Al_2O_3/Li_2O replacement have been examined. The coefficients of thermal expansion were determined at different temperatures to detect the local structure changes induced by MnO, and its contribution with CaO and MgO to the thermal expansion of both glass and crystalline solids.

The addition of MnO replacing CaO decreases the thermal expansion of the glasses, while MnO/MgO replacement increases this property. A large, abrupt decrease in the expansion coefficient of the glasses was observed following Al_2O_3/Li_2O replacement.

On crystallisation, the expansivity of the glasses was markedly changed. It was greatly affected by crystallization of various Mn-silicate varieties and/or aluminosilicate solid solutions.

Correlation between the expansion data and the contribution of the incorporated cations in the glass structure as well as the crystal phase composition of the crystalline solids are discussed.

INTRODUCTION

The properties of silicate glasses containing transition metal ions have received the attention of many workers who have investigated the contributions of these ions to the crystallisation, thermal, electrical and other physical properties of the glasses [1–5]. Manganese glasses, however, have received little such attention.

Thermal expansion is one of the most important properties of glass and glass-ceramic materials, as it directly or indirectly affects all the commercially important properties of glass and is often extremely influential in restricting the usefulness of a particular glass composition. A thorough understanding of this property is important, as it can lead to the development of new glasses with selected properties.

The thermal expansion of glass is closely correlated with the cation constituents of the glass, and their influence on the formation of the internal structure [6–8].

TABLE 1

Chemical composition and thermal expansion coefficient values of the glasses

Glass no.	Oxides (mol.%)						Expansion coefficients ($^\circ C^{-1} \times 10^{-7}$)	
	Li_2O	MgO	CaO	MnO	Al_2O_3	SiO_2	20–300 °C	20–400 °C
1	23.12	–	13.28	–	–	63.6	97.5	101.3
2	23.12	–	9.96	3.32	–	63.6	93.57	89.9
3	23.12	–	6.64	6.64	–	63.6	91.07	96.2
4	23.12	–	3.32	9.96	–	63.6	–	–
5	23.12	13.28	–	–	–	63.6	75.7	82.32
6	23.12	6.64	–	6.64	–	63.6	82.1	89.4
7	23.12	3.32	–	9.96	–	63.6	87.5	93.75
8	23.12	3.32	6.64	3.32	–	63.6	88.98	95.01
9	11.56	3.32	6.64	3.32	11.56	63.6	44.5	51.5
10	9.25	3.32	6.64	3.32	13.87	63.6	39.01	44.96

The heat treatment of glasses introduces crystalline phases which have expansion coefficients that are markedly different from those of the parent glasses. An extremely wide range of expansion coefficients is covered by the different crystalline or solid solution phases, and the development of these phases in appropriate proportions forms the basis of the production of glass-ceramics with controlled thermal expansion coefficients [9–11].

The aim of the present work is to report the thermal expansion characteristics of some Mn-containing silicate materials in order to indicate the changes in the thermal expansion coefficients that can result from the presence of MnO in glass or crystalline solids.

EXPERIMENTAL

The thermal expansion properties of some lithia silicate glasses containing various MnO/CaO and MnO/MgO ratios together, in some cases, with Al_2O_3/Li_2O replacement have been investigated. The glass compositions are given in Table 1.

Material preparation

The glass batches were prepared from purified, pulverised silica sand, AnalaR grades of Li_2CO_3, $CaCO_3$, $MgCO_3$, calcinide alumina and high purity MnO, as the source of MnO. They were melted in fireclay crucibles in a gas-fired furnace at 1300–1450 °C for 3 hours. The glass melts were cast into rectangular slabs (1 × 1 cm^2 in cross-section and 5–7 cm long); then they were well annealed to minimise strain.

Selected heat-treatment regimes for the glasses were used to obtain glass-ceramics having minimum residual glassy matrix without deformation. The Al_2O_3-free glasses, therefore, were soaked at 500 °C for 2 h and then at 800 °C for 8 h, whereas the Al_2O_3-containing glasses were soaked at 650 °C for 3 h and then at 850 °C or 950 °C for 8 h, depending on the Al_2O_3 content of the glass. X-ray diffractometry using a Ni filter and Cu radiation was used to identify the crystalline and solid solution phases formed.

Thermal expansion measurements

The linear thermal expansion values of the glass and crystalline solids were measured using a calibrated vitreous silica dilatometer. Specimen rods were heated at a rate of 10 °C min^{-1} and elongation was followed by a gradual dial gauge (sensitivity 0·001 mm). Data were obtained for each glass specimen from room temperature up to 440 °C, while for the corresponding crystalline solids, the measurements were extended up to 800 °C using the same heating rate. At least two measurements were made for each specimen to obtain reproducible results. The linear thermal expansion coefficient was then calculated using the equation

$$\alpha = \left(\frac{\Delta L}{L \Delta t} + 0.54 \right) \times 10^{-7} \tag{1}$$

where ΔL is the increase in the original length L of the specimen, while Δt is the increase in temperature. The last term (0.54) represents the correction factor for the expansion of quartz tube.

RESULTS

The expansion coefficients (α) of the glasses and crystalline solids are given in Tables 1 and 2 respectively. The thermal expansion curves and the compositional dependence of the expansion coefficient of the glasses and crystalline solids are shown in Figs. 1–6. The data obtained yielded the following conclusions.

Thermal expansion data of the glasses

The expansion curves of the glasses (Figs. 1, 3 and 5) are generally similar to those characteristic of most silicate glasses. Most of these curves have slight curvatures with the expansion coefficient (α) of the glasses being almost a function of the compositional modification taking place. Figure 2, clearly indicates that the partial replacement of CaO by MnO decreases the α values of the glasses. Table 1 shows that the expansion

TABLE 2

Phases developed and thermal expansion coefficient values of the crystalline solids

Glass no. [a]	Phases developed [b]	Expansion coefficient ($^\circ C^{-1} \times 10^{-7}$)		
		20–300 °C	20–400 °C	20–800 °C
C_1	LS_2, Wo, α-Qz (m)	85.95	92.07	107.9
C_2	LS_2, Mn-Wo, α-Qz (m)	82.8	88.1	106.5
C_3	LS_2, bustamite, α-Qz (m)	78.22	85.3	103.96
C_4	LS_2, β-Mn-Ca-silicate, α-Qz (m)	73.01	82.62	101.74
C_5	LS_2, C, α-Qz (m)	62.58	71.6	95.11
C_6	LS_2, kanoite, α-Qz	67.77	75.69	99.05
C_7	LS_2, rh.ss., α-Qz	70.7	78.91	100.98
C_8	LS_2, Mn-pyroxene ss., α-Qz	68.4	76.06	99.8
C_9	β-ep., Mn-pyroxene ss.	7.89	9.66	18.86
C_{1-10}	β-euc., β-spod., Mn-pyroxene ss.	4.28	6.08	12.52
C_{2-10}	β-spod., Mn-pyroxene ss.	5.71	10.21	16.37

[a] C_1–C_8 heated at 500 °C for 2 h and 800 °C for 8 h.; C_9 and C_{1-10} heated at 650 °C for 3 h and 850 °C for 8 h; C_{2-10} heated at 650 °C for 3 h and 950 °C for 8 h.

[b] LS_2, lithium disilicate; Qz, quartz; Wo, wollastonite; C, clinoenstatite; Rh., rhodonite; spod, spodumene; euc, eucryptite; m, minor; and ss., solid solution.

coefficient of the lithia-calcia-silicate glass (G_1) is decreased by successive additions of MnO at the expense of CaO (G_2, G_3). On the other hand, the addition of MnO replacing MgO progressively increases the expansion coefficient of the glasses (Fig. 4). It can be seen from Table 1 that the α value of G_5 (with MgO) is lower than that of G_7 (with MnO instead of MgO).

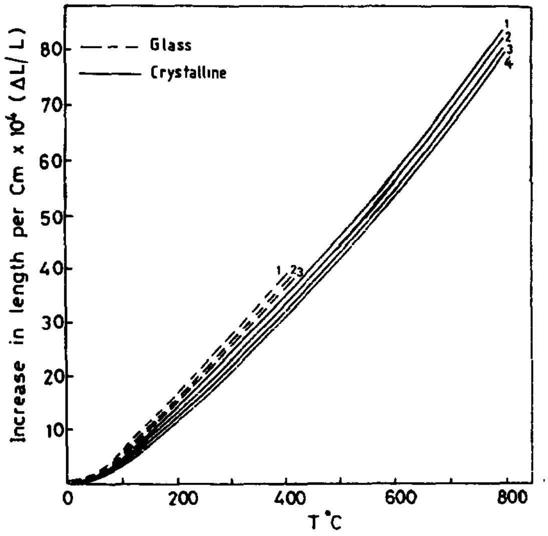

Fig. 1. Linear thermal expansion curves of MnO/CaO glasses and their crystalline solids.

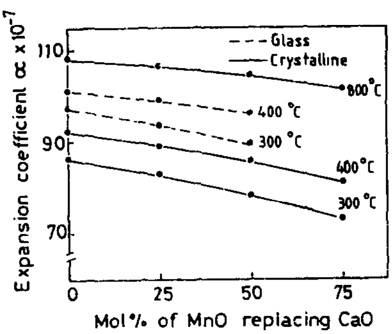

Fig. 2. Change in expansion coefficient of glasses and crystalline solids as a function of MnO/CaO replacement.

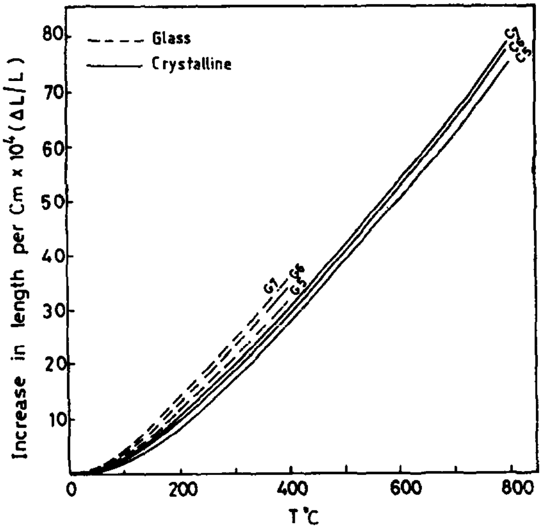

Fig. 3. Linear thermal expansion curves of MnO/MgO glasses and their crystalline solids.

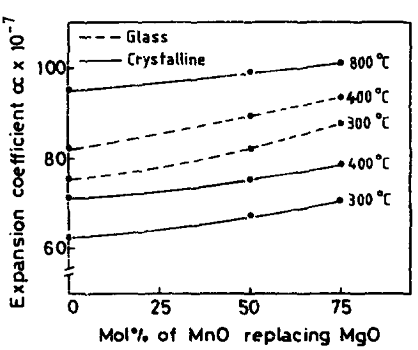

Fig. 4. Changes in expansion coefficient of glasses and crystalline solids as a function of MnO/MgO replacement.

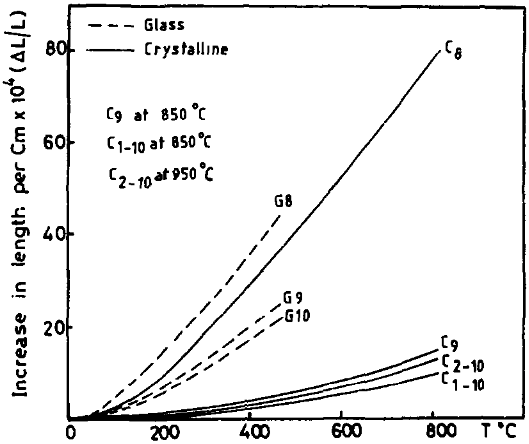

Fig. 5. Linear thermal expansion curves of MnO and Al_2O_3/Li_2O glasses and their crystalline solids.

However, for the Al_2O_3-containing glasses, it is evident that Al_2O_3/Li_2O replacement greatly decreases the α values of the glass (Fig. 5). Table 1 clearly indicates that the α values of the glasses are greatly lowered by addition of Al_2O_3 instead of Li_2O (G_8, G_9, G_{10}).

Crystal phases and solid solution formed

Lithium disilicate and wollastonite ($CaSiO_3$), together with minor α-quartz, were formed in lithia-calcia-silicate glass ceramics (C_1, Fig. 7).

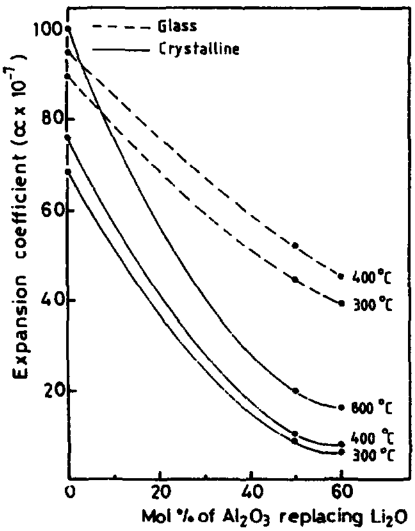

Fig. 6. Changes in expansion coefficient of glasses and crystalline solids as a function of Al_2O_3/Li_2O replacement.

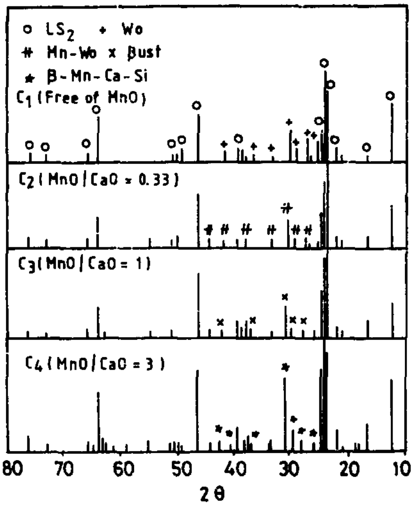

Fig. 7. XRD data of crystalline solids with various MnO/CaO ratios.

However, varieties of Ca,Mn-silicate phases were identified for the glass ceramics of various MnO/CaO ratios. At low MnO/CaO ratio (C_2), Mn-wollastonite ($Ca_{0.75}Mn_{0.25}SiO_3$) was formed. Increasing the MnO/CaO ratio in the glass up to unity, (C_3), yielded bustamite ($CaMnSi_2O_6$). At higher MnO/CaO ratios (C_4, Fig. 7), β-$Mn_{0.75}Ca_{0.25}SiO_3$ phase was identified. In all cases studied, predominant lithium disilicate ($Li_2Si_2O_5$) and minor alpha quartz were formed.

The X-ray diffractogram also indicated that clinoenstatite, lithium disilicate and minor α-quartz were crystallised from lithia-magnesia-silicate glass (C_5, Fig. 8). On partial MnO/MgO replacement, various Mn,Mg-silicate solid-solution phases were crystallised in the glasses (C_6, C_7, Table 2, Fig. 8). Kanoite, the Mn-containing phase of clinopyroxene of the type $Mn^{2+}Mg$ (Si_2O_6), was crystallised by increasing the MnO/MgO ratio in

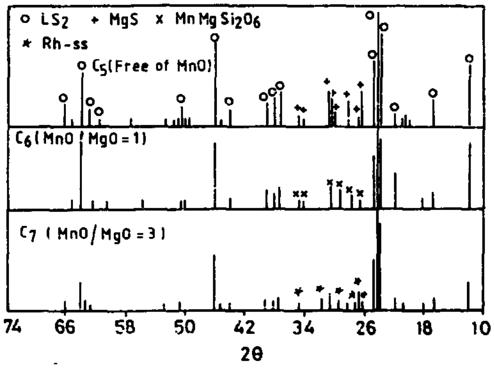

Fig. 8. XRD data of crystalline solids with various MnO/MgO ratios.

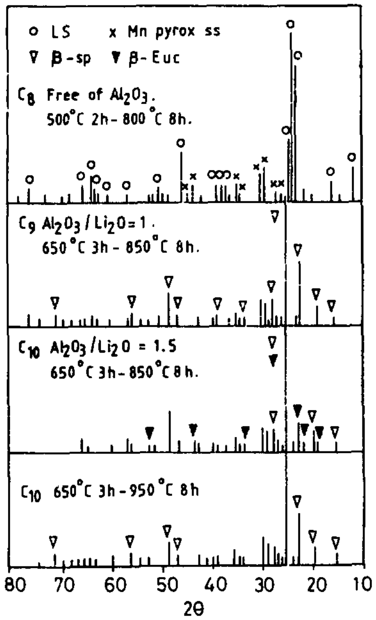

Fig. 9. XRD data of crystalline solids with constant MnO and various Al_2O_3/Li_2O ratios.

the glass up to unity (C_6, Fig. 8). At higher MnO/MgO ratios, a rhodonite solid solution phase $(Mn_{0.75}Mg_{0.25})$ SiO_3 was encountered (C_7, Fig. 8). Lithium disilicate and an Mn-pyroxene-like phase of probable formula $(Ca^{2+})(Mn^{2+}_{0.5}Mg^{2+}_{0.5})$ Si_2O_6 were formed in the lithia silicate glass-ceramics in which CaO, MnO and MgO are present (C_8, Fig. 9).

However, the partial replacement of Al_2O_3 for Li_2O favours the formation of a lithium aluminosilicate solid solution, (β-eucryptite and/or β-spodumene ss.) at the expense of $Li_2Si_2O_5$(C_9–C_{10}, Fig. 9). β-Eucryptite was formed together with β-spodumene from the glass at low temperature (C_{1-10}, Fig. 9), while at higher temperatures, β-spodumene only was recorded (C_{2-10}, Fig. 9).

Thermal expansion of the crystalline solids

The thermal expansion curves of the crystalline solids are recorded in Figs. 1, 3 and 5, while the variation of the mean linear expansion coefficient as a function of MnO or Al_2O_3 content is given in Figs. 2, 4 and 6. The calculated linear expansion coefficients are given in Table 2.

The present results show that the expansion coefficients of the crystalline solids were generally much lower than those of the corresponding glasses. The partial replacement of CaO by MnO in lithia-calcia silicate glass-ceramics decreases the α values of the material, as indicated from Fig. 2 where a progressive decrease of the α values of the crystalline solids is observed on addition of MnO replacing CaO. The expansion coefficient of specimen C_1 (free of MnO) has the highest value, while sample C_4 (with the highest MnO content) has the lowest α value.

However, the thermal expansion coefficient of the lithia-magnesia silicate glass-ceramics was increased by addition of MnO instead of MgO. The change in thermal expansion as a function of MnO/MgO ratio in the glass (Fig. 4) shows that the α value is lowest for crystalline solids free of MnO (C_5, Table 2) and that it increases with increasing MnO/MgO replacement.

A large decrease in the α values of the crystalline solids was recorded on addition of Al_2O_3 instead of Li_2O. Figure 6 clearly shows that a large decrease in the expansion coefficient of the material was recorded on addition of Al_2O_3 replacing Li_2O, up to Al_2O_3/Li_2O ratios of unity. Beyond this ratio, some fluctuation in the α values was observed.

Table 2 indicates that the α values of samples C_9 and C_{1-10}, with Al_2O_3/Li_2O ratios of 1 and 1.5 respectively, are lower than that of sample C_8 (free of Al_2O_3), the α value of sample C_{1-10} being the lowest. However, the treatment of sample C_{2-10} (Al_2O_3/Li_2O ratio 1.5) at higher temperatures (950 ° C), gave increased α values.

DISCUSSION

Like many substances, glass expands in proportion to any increase in temperature and contracts when cooled; the magnitude of the change varies according to the composition.

In addition, the volume of a material increases with increasing temperature because of the increasing amplitude of vibration of the atoms associated with changing interatomic distances and bond angles. In glass, this mechanism alone is responsible for the flat straight-line section of the expansion curve which extends up to the lower annealing temperature and determines the end of the region of elastic behaviour. In this range, the thermal expansion of a glass is much the same as that of crystalline material of the same composition [12].

The thermal expansion of glass is not only a function of temperature but also depends, among other factors, on composition. The thermal expansion is also sensitive to the structure of the glass, e.g. degree of polymerisation, type of structural units, the nature and contribution of the different cations, whether they occupy forming or modifying positions in the glass network. Accordingly, thermal expansion data can yield valuable information regarding, for example, the structural changes induced by modification of composition or heat treatment [8].

To discuss the effect of adding a transition metal oxide, such as MnO in replacing CaO or MgO, on the thermal expansion property of the glasses, the role of such oxides in the geometrical arrangement of the building units of the glassy network must be considered.

It is logical to assume that the introduction of non-bridging oxygen ions decreases the coherency of the network in the glass structure and, consequently, increases the expansion coefficient. In particular, the nature of the divalent cations should be taken into consideration and it has been suggested [13] that the bond strength and the nature of the bond of the divalent cation with oxygen govern the thermal expansion. An open, less rigid or loose structure favours an increase in the thermal expansion and a decrease in the transformation and softening temperatures. The loosening of the Si–O bond is more apparent with the larger Ca ions (0.99 Å) than with Mn ions (0.8 Å). The former will acquire a lower field strength than the latter. It is expected, therefore, that MnO/CaO replacement will decrease the thermal expansion coefficient of the glass. This is agreement with the results obtained by Kumar and Nath [14].

On the other hand, the smaller cations with higher field strength seem to produce more strongly bond structures than the larger cations; and the smaller cation glasses are generally characterised by larger moduli and smaller expansion coefficients [15]. The binding energy increases with increasing valency and decreasing size of the atom [6]. The thermal expansion is also assumed to increase as the amount of ionic bonding increases [7]. Also, the ability of some divalent ions, (e.g. Mg^{2+}), to participate in the glass structure as network tetrahedral units, while others, e.g. Mn^{2+}, have an interstitial position, has to be considered.

To explain why the addition of MnO replacing MgO in the alkali silicate glasses studied increases the thermal expansion coefficient, we suggest that the Mn^{2+} ions formed in these silicate glasses, of reducing melting condition, exhibit an octahedral coordination state with oxygen [16]. These octahedral Mn^{2+} groups possess a lower field strength (3.125) than that of Mg^{2+} in tetrahedral coordination (4.73). It is expected, therefore, that the addition of MnO at the expense of MgO increases the thermal expansion coefficient of the glasses.

In alumino silicate glass, both the tetrahedral AlO_4 group and the octahedral AlO_6 group can be formed. In the present glass, aluminium of tetrahedral coordination (AlO_4) was preferentially formed. At low Al_2O_3/Li_2O replacement, the Al^{3+} coordination seems to change to four coordination, due to the oxygen present, with lithium occupying the interstices. This is associated with a change in bonding character with a simultaneous increase in the tightness of the structure, resulting in a progresive decrease in the expansion coefficient of the glass. Dietzel [17] explained similar results by assuming that the field strength becomes stronger by including Al_2O_3 in silicate glasses. With a further increase in the Al_2O_3 content, there is a possibility of a decrease in non-bridging. 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 Al^{4+} in tetrahedral coordination might explain the abrupt, progressive decrease in the thermal expansion coefficient with high Al_2O_3 content in the glass.

The thermal expansion of crystalline solids can be markedly different from those of the parent glasses. The crystallisation process greatly alters the thermal expansion of the glasses. The data obtained are a direct function of the nature of the crystal phases formed and the residual glassy matrix [18]. If the α values for glasses vary uniformly with their chemical composition, the α values for crystalline solids, such as glass-ceramics, depend mainly on the α values of the primary crystalline and complementary glassy phases [9]. In most cases, the expansion coefficient of the crystalline materials generally increases with increasing glass phase content [18].

An extremely wide range of thermal expansion coefficients is covered by the different crystal types and the development of these phases in appropriate proportions forms the basis of the production of glass-ceramics with controlled thermal expansion coefficients. It has been reported that pyroxenes, wollastonite and lithium silicate phases have high positive values of their expansion coefficients. Diopside and clinoenstatite which are considered to be pyroxene-type have α values of $50–150 \times 10^{-7}\,°C^{-1}$ (20–1000 °C) [19] and $135 \times 10^{-7}\,°C^{-1}$ (300–700 °C) [20] respectively. Wollastonite has a value of $94 \times 10^{-7}\,°C^{-1}$ (100–200 °C) [21] while lithium disilicate has a value of $110 \times 10^{-7}\,°C^{-1}$ (20–600 °C) [18].

On the other hand, crystallisation of lithium aluminosilicate glasses generally produces crystal phases such as β-eucryptite and/or β-spodumene with much lower expansion coefficients than those of the parent glasses. Both β-eucryptite and the composition corresponding to Li_2O–Al_2O_3–$3SiO_2$ have negative coefficients of expansion [10]. β-Eucryptite has a high negative expansion of -86×10^{-7} (20–700 °C) [18]. The expansion coefficients of β-spodumene and its solid solution have low positive values from 3×10^{-7} to $9 \times 10^{-7}\,°C^{-1}$, in accordance with the relative proportion of spodumene, quartz or cristobalite phases [18].

According to the previous considerations, it follows, therefore, that the progressive decrease in the α values of the crystalline solids caused by addition of MnO instead of CaO (samples C_2, C_3 and C_4) may be attributed to the formation of Mn-containing phases, e.g. Mn-wollastonite, bustamite and β-Mn-Ca-silicate, instead of the high-expanding wollastonite phase formed in sample C_1.

The contribution of a particular crystal phase to the thermal expansion of a glass-ceramic may be modified if the crystal phase enters into solid solution with another phase [18]. There is no available data for the expansion coefficient of the $MnSiO_3$ phase but a more significant fact is that a continuous solid solution series between rhodonite ($MnSiO_3$) and clinoenstatite ($MgSiO_3$) could be formed, and a variety of pyroxene solid solutions can be obtained depending on the MnO/MgO ratio in the glass. Actually crystalline pyroxene phases have relatively high coefficients of thermal expansion. It is suggested, therefore, that the increase in the α values of the resulting crystalline solids caused by MnO/MgO replacement in the glass may be due to the formation of Mn solid-solution varieties, including the high-expanding pyroxene solid-solution phases.

In the Al_2O_3-containing variety, the very low-expanding β-spodumene solid-solution phase, was formed at the expense of the relatively very high-expanding lithium disilicate phase (C_8, C_9; Table 2). For this reason the replacement of Li_2O by Al_2O_3 in the glass (G_9) up to an Al_2O_3/Li_2O ratio of unity decreases progressively, to a great extent, the α values of the corresponding crystalline solid (C_9).

A progressive decrease in the α value of the Al_2O_3-containing sample is also observed on further Al_2O_3/Li_2O replacement, i.e. $Al_2O_3/Li_2O > 1$. This may be attributed to the formation of the β-eucryptite together with the β-spodumene solid solution phases in the material (C_{1-10}). However, at higher temperatures the thermal expansion of the sample is increased. The thermal expansion characteristics of a glass-ceramic can be markedly affected by the heat treatment schedule as this determines the proportions and nature of the crystal phases present. This is illustrated strikingly by comparison of the curves of samples C_{1-10} and C_{2-10} in Fig. 5. Both of these glass-ceramics were prepared from the same parent glass composition, so that chemically they are identical. In one case, however, the heat treatment produced both β-eucryptite and β-spodumene solid solution as major constituents together with Mn-pyroxene, while in the other, high-temperature case, all the β-eucryptite was transformed to the β-spodumene solid solution phase.

REFERENCES

1 S.M. Salman, Thermochim. Acta, 81 (1984) 125.
2 N.A. Ghoneim, A.A. Ahmed and S. Gharib, Thermochim. Acta, 71 (1983) 43.
3 S.N. Salama, Mater. Chem. Phys., 26 (1990) 285.
4 S.M. Salman and S. Gharib, Thermochim. Acta, 77 (1984) 227.
5 K. Zirkelbach and R. Bruckner, Glastech. Ber. 60 (9) (1987) 312.
6 K. Takahashi, J. Soc. Glass Technol., 37 (1953) 3.
7 M.D. Karkhanavala and F.A. Hummel, J. Am. Ceram. Soc. 35 (9) (1953) 215.
8 W.A. Weyl and E.C. Marboe, The Constitution of Glasses, A Dynamic Interpretation, Vol. 1, Academic Press, New York, 1962, p. 353.
9 A.I. Berezhnoi, Glass Ceramics and Photositals, Plenum Press, New York, 1970, p. 315.
10 F.A. Hummel, J. Am. Ceram. Soc., 8 (1951) 235.
11 S.N. Salama, Thermochim. Acta, 164 (1990) 91.
12 D.G. Holloway, The Physical Properties of Glass, Wykeham Publications, London, 1973.
13 A.A. Ahmed, A.F. Abbas and S.M. Salman, Phys. Chem. Glasses, 36 (1) (1985) 17–23.

14 S. Kumar and P. Nath, Trans. Indian Ceram. Soc., 24(4) (1965) 127.
15 D.R. Uhlmann and D.R. Shaw, J. Non-Cryst. Solids, 1 (1969) 347.
16 W.A. Weyl, Coloured Glasses, Soc. Glass Technol. Sheffield, England, 1951.
17 A. Dietzel, Glastech. Ber., 22 (1948) 42.
18 P.W. McMillan, Glass-Ceramics, Academic Press, London 1979, p. 222.
19 L.W. Finger and Y. Ohashi, Am. Mineral, E, (1974) 303.
20 J.F. Sarver and F.A. Hummel, J. Am. Ceram. Soc., 25 (4) (1962) 152.
21 G.R. Rigby and A.T. Green, Trans. Br. Ceram. Soc., 41 (1942) 41.