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THERMAL EXPANSION CHARACTERISTICS OF SOME IRON-CONTAINING GLASSES AND THEIR CORRESPONDING CRYSTALLINE MATERIALS

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ABSTRACT

The thermal expansion of some lithium silicate glasses containing varying proportions of Fe_2O_3 (replacing silica) has been investigated before and after thermal treatment.

The coefficient of thermal expansion of the glasses at different temperatures, the transformation and dilatometric softening temperatures were determined to detect local structural changes that might be induced by the Fe_2O_3/SiO_2 replacement. The experimental results and anomalies observed were related to different views concerning the change in the valency and state of coordination of iron with its concentration in the glass, and to the phase separation that might develop in lithium silicate glasses.

In the crystalline state, the expansion coefficient was measured from room temperature up to 700 °C for various iron-containing samples, and the data obtained were correlated to the type and content of the mineral phases formed as indicated by the X-ray technique.

INTRODUCTION

The properties of iron-containing silicate glasses have drawn the attention of many workers to investigate the role played by iron in the glass structure and its effect on the thermal, electrical, crystallization and other physical properties [1–4].

The thermal expansivity is one of the first properties found to be characteristic of the glassy state. The expansion curves of glasses are very similar and have been used for determining T_g, the temperature at which the supercooled liquid changes into a glass [5]. Thermal expansion is an important property which has to be considered in the formulation of glass compositions, and in many practical applications of glasses. It determines the range of materials to which a glass can be safely sealed and it affects the ability of the glass to survive thermal shock or cycling. Thermal expansion is a complex property connected with the magnitude and distribution of forces acting in the system, and reflects any change of the distribution of forces with increasing thermal vibration [5].

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The coefficient of linear thermal expansion generally depends on the temperature, composition and thermal history of the glass. The composition of a glass influences its structure. The thermal expansion is therefore sensitive to the structure of a glass, e.g., degree of polymerization, structural units and the nature and role played by the different cations, whether to occupy a network forming or modifying position in the network. Accordingly, thermal expansion data can yield valuable information regarding structural changes induced by composition modifications or heat-treatment.

The thermal expansion coefficient of glass-ceramic or polycrystalline materials can be markedly different from that of the parent glass. The process of crystallization introduces phases which have coefficients of thermal expansion that are usually different from that of the parent glass, and the glass-ceramic may have a higher or lower coefficient of expansion depending on the crystal phases formed [6].

In the present work, the thermal expansion of some iron-containing glasses have been investigated before and after heat-treatment. The composition of the glasses is based on the Li_2O–SiO_2 system in which the SiO_2 was partly replaced' by iron oxide. The present experimental investigation was conducted to gain insight into the role of iron in building the network of the glass structure, and in the formation of the phases developed in the corresponding crystalline material and the reflection of these effects on the thermal expansion behaviour of such a glass composition.

EXPERIMENTAL

Glass preparation

The glass compositions are given in Table 1. Glass batches were prepared from AnalaR and reagent grade lithium carbonate and ferric oxide (red, anhydrous). Silica was introduced as pulverized and purified quartz. Mixed

TABLE 1

Thermal expansion data of the glasses investigated

Glass No.	Glass composition (mol%)			Original length, L (cm)	α($^\circ C^{-1} \times 10^{-6}$) 100–300 °C	T_g (°C)	T_s (°C)
	Li_2O	SiO_2	Fe_2O_3				
G_1	34.83	65.17	—	2.765	12.8	450	480
G_2	34.83	64.17	1	3.525	13.4	447	478
G_3	34.83	63.17	2	3.015	13.8	435	471
G_4	34.83	62.17	3	3.455	12.5	440	476
G_5	34.83	61.17	4	3.395	12.3	439	475
G_6	34.83	60.17	5	3.320	12.8	432	467
G_7	34.83	59.17	6	3.475	11.6	447	483

glass batches were melted in platinum–2% rhodium crucibles in a muffle electric furnace at a temperature of 1350 °C for 4 h with occasional stirring for complete homogeneity. The melt was then cast as rods of the required dimensions and properly annealed to room temperature.

Glass-ceramic preparation

For obtaining crystalline materials, some of the glass specimens were thermally treated by applying two types of heat-treatment regimes:

(a) one-step, i.e., at 700 °C for 2 h;

(b) two-steps, i.e., at 500 °C for 6 h and then at 850 °C for 10 h.

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

Thermal expansion measurements

For thermal expansion measurements, a rod specimen approximately 0.5 × 0.5 × 3.5 cm was required. The ends and the whole bulk of the glass were ground and parallel. The dimensions of the glass and glass-ceramic specimens were measured with a high precision micrometer which was read to three decimal places.

A Netzsch Dilatometer type 402 Ep (W. Germany) was used for the measurement of the glass expansion from room temperature to above the softening temperature with a heating rate of 10 °C min^{-1}. Meanwhile, in the crystalline state, the expansion was measured from room temperature up to 700 °C applying the same heating rate.

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

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

where L is the original length of the specimen, ΔL is the increase in length, and ΔT is the increase in temperature. The last term of this equation is the correction factor for the expansion of the quartz tube.

RESULTS

Thermal expansion data of the glasses

The thermal expansion curves of all the glasses have been recorded (Fig. 1). Table 1 includes the coefficient of expansion (α) as well as the dilatometric transformation (T_g) and softening (T_s) temperatures of the glasses studied. Figure 2 reports the variation of the coefficient of expansion (α) with Fe_2O_3

content of the glasses in comparison with the corresponding variations in T_g and T_s.

The experimental thermal expansion data of the glasses studied, as shown in Fig. 2 and Table 1, reveal the following outlines.

The expansion curves for all the glass compositions show similar characteristics. During the first 25–50 °C of heating, the expansion of the specimen is quite small. This is probably due to the time it took for the heat to penetrate through the quartz tube before starting to heat the specimen. In general, the thermal expansion of the glasses can be considered as a linear function of temperature up to at least 400 °C (Fig. 1), after which they are

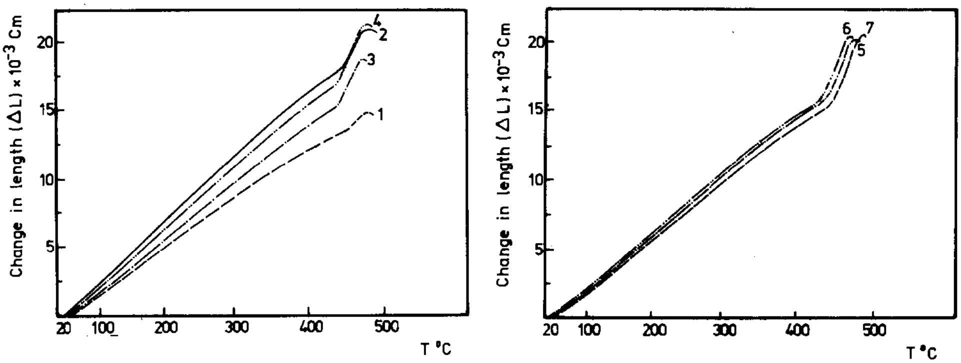

Fig. 1. Linear thermal expansion curves of iron-containing glasses.

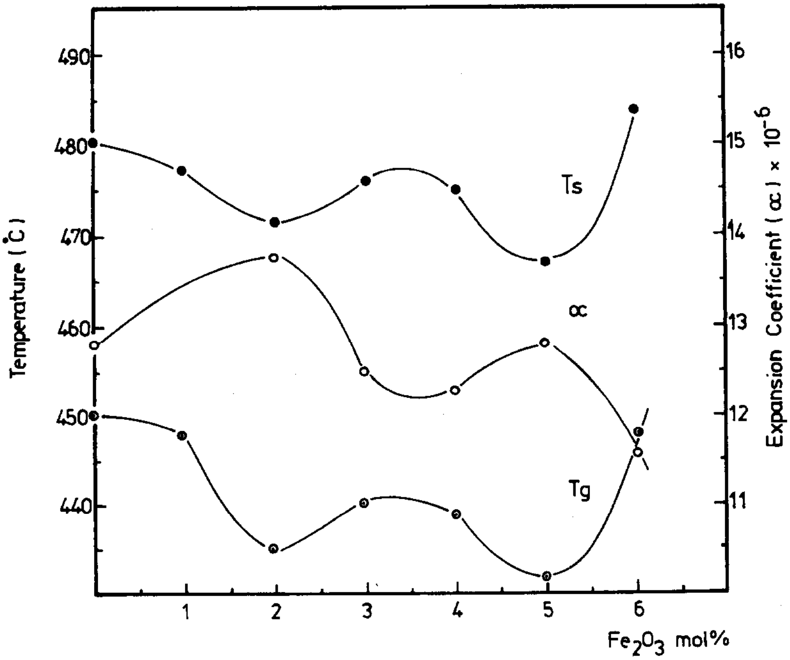

Fig. 2. Change of linear thermal expansion coefficient (α), dilatometric softening (T_s) and transformation (T_g) temperatures as a function of Fe_2O_3 content in the glasses.

no longer linear. This may be referred to as the transformation range of the glass, which a well-documented phenomenon in various glasses [7].

The study of mean linear thermal expansion coefficient values between 100–300 °C, and the dilatometric transformation (T_g) and softening (T_s) temperatures of the various glasses as determined from Fig. 1, revealed that an Fe_2O_3/SiO_2 replacement of up to 2 mol% seems to increase the α values of the glasses, while both the T_g and T_s values decrease (Fig. 2). However, at higher iron oxide contents in the glass, some fluctuation in the thermal expansion data is observed; with further Fe_2O_3/SiO_2 replacement of up to 4 mol% Fe_2O_3, the values tend to decrease and both T_g and T_s increase. At 5 mol% Fe_2O_3 replacement for silica, the α values of the glass seem to be increased, but it extends to a lower value than those for glasses containing up to 2 mol% Fe_2O_3. Meanwhile, with an increase of iron oxide content in the glass to 6 mol%, the α values again decrease and consequently an increase in the T_g and T_s temperatures is observed.

X-ray investigation of the crystallized glasses

Figures 3 and 4 represent the X-ray diffraction patterns of the glass-

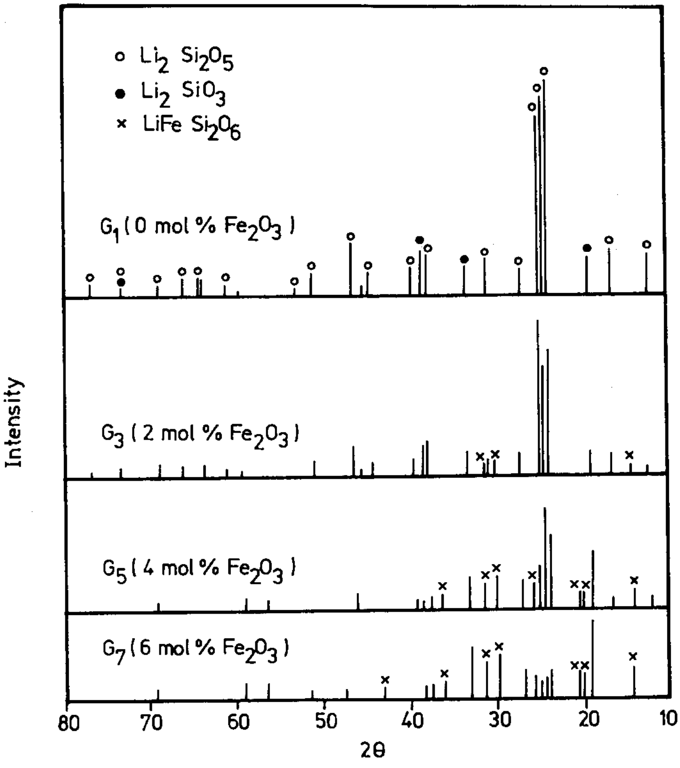

Fig. 3. X-ray diffraction data of the glasses crystallized at 500 °C for 6 h, 850 °C for 10 h.

ceramics. It is evident that lithium disilicate ($Li_2Si_2O_5$), lithium metasilicate (Li_2SiO_3) and lithium iron silicate ($LiFeSi_2O_6$) were the main phases which crystallized from the glasses after different thermal treatments. As the iron content in the glass is increased (replacing silica), lithium iron silicate and lithium metasilicate are increased, while lithium disilicate is decreased. The crystallization process and the sequence of phases deposited in the present glasses has been previously investigated in detail [4].

In fact, as seen by the X-ray investigation (Fig. 3), the intensity of the diffraction lines of both the $LiFeSi_2O_6$ and Li_2SiO_3 formed increase at the expense of the intensity of the diffraction lines of lithium disilicate.

Figure 3 shows that the characteristic lines of the $LiFeSi_2O_6$ phase are only detected in the glass-ceramic materials containing more than 1 mol%

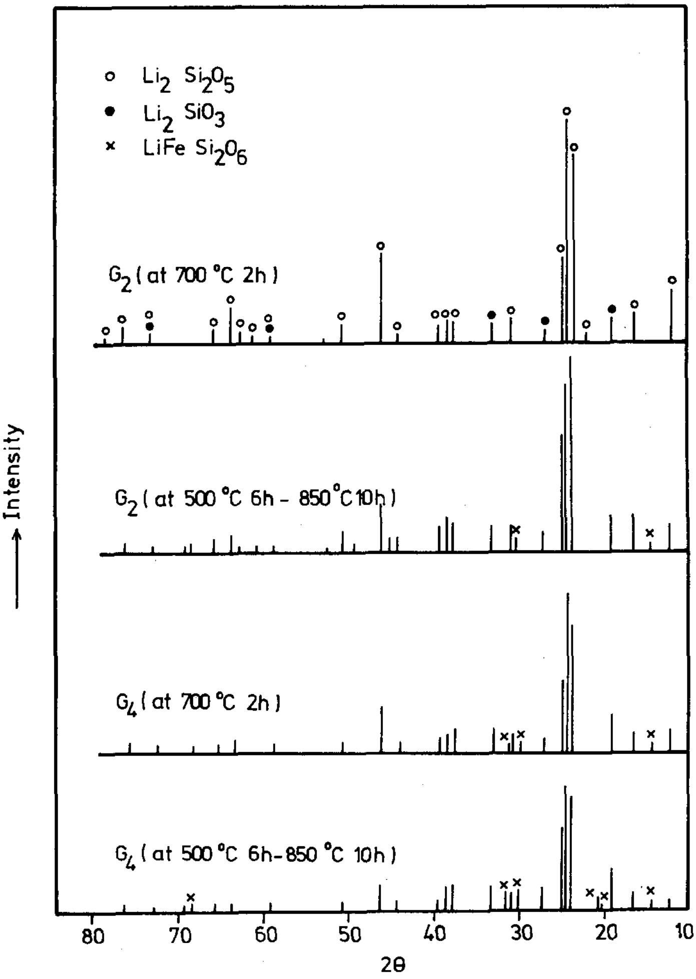

Fig. 4. X-ray diffraction data of: glass 2 (1 mol% Fe_2O_3) and glass 4 (3 mol% Fe_2O_3).

Fe_2O_3. The diffraction lines of this phase increase with increasing iron oxide content in the materials. It is also evident (Figs. 3 and 4) that the increases in the temperature favour the crystallization of the alkali iron silicate phase ($LiFeSi_2O_6$).

Thermal expansion data of the glass-ceramics

The thermal expansion curves of the glass-ceramic specimens have been recorded in Figs. 5 and 6, while the variation of the mean linear expansion coefficient as function of iron oxide content are represented in Fig. 7. The calculated linear thermal expansion coefficients are given in Table 2. The results obtained indicate that the replacement of SiO_2 by iron oxide in the glasses progressively increases the α values of the corresponding crystalline materials (glass-ceramics). The thermal expansion coefficient of specimen C_1, (free of iron) represents the lowest values, while that of sample C_7 (with 6 mol%) being the highest. Figure 7 clearly indicates the dependence of the thermal expansion of the glass ceramics on the iron content of the materials. The results also indicate that the thermal expansion of the crystalline materials are temperature dependent. It is evident that the mean linear thermal expansion coefficients of the glasses thermally treated at 700 °C (C_2' and C_4') are greater than those of the same glasses heat-treated through the two-step regime (i.e., 500 °C for 6 h, 850 °C for 10 h).

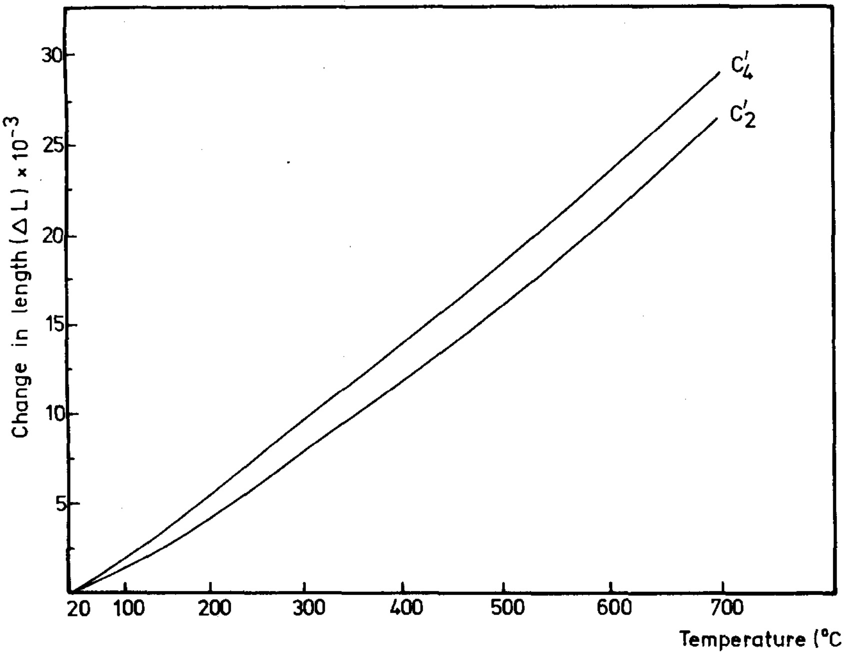

Fig. 5. Linear thermal expansion curves of some iron-containing glasses treated at 700 °C for 2 h.

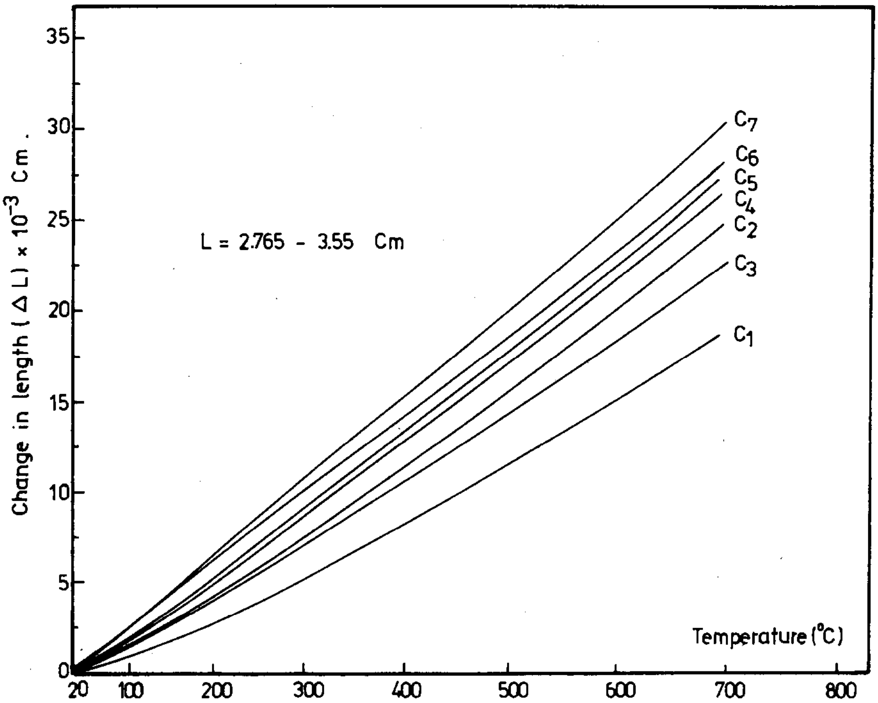

Fig. 6. Linear thermal expansion curves of various iron-containing glasses treated at 500 °C for 6 h, 850 °C for 10 h.

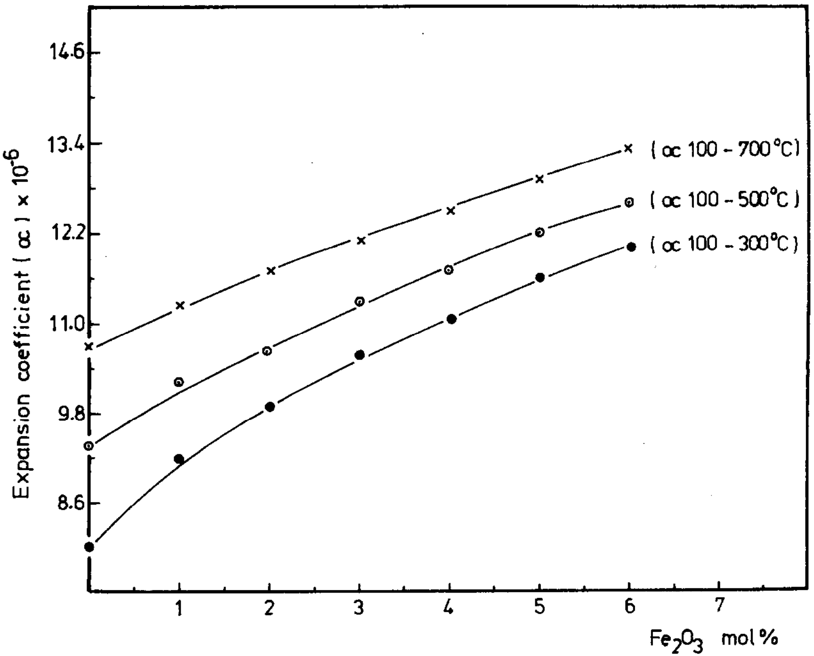

Fig. 7. Compositional dependence of linear thermal expansion coefficient (α) of the crystalline materials at different temperature ranges.

TABLE 2

Thermal expansion data of the crystalline materials (glass-ceramics)

Sample[a] No.	Fe_2O_3 (mol%)	Phases developed[b]	$\alpha(^\circ C^{-1} \times 10^{-6})$		
			100–300 °C	100–500 °C	100–700 °C
C_1	0	Ls_2, Ls(m)	8.0	9.4	10.7
C_2'	1	Ls_2, Ls(m)	9.5	10.6	11.8
C_2	1	Ls_2, Ls, LFs(m)	9.2	10.2	11.25
G_3	2	Ls_2, Ls, LFs	9.9	10.6	11.7
C_4'	3	Ls_2, Ls, LFs(m)	11.4	11.9	12.9
C_4	3	Ls_2, Ls, LFs	10.6	11.3	12.1
C_5	4	Ls, Ls_2, LFs	11.05	11.7	12.5
C_6	5	Ls, LFs, Ls_2	11.6	12.2	12.9
C_7	6	Ls, LFs, Ls_2	12.0	12.6	13.3

[a] The glasses were treated by the two-step regime (500 °C for 5 h, 850 °C for 10 h) except those of samples C_2' and C_4', which were thermally treated at 700 °C for 2 h.

[b] Ls_2 = lithium disilicate; Ls = lithium metasilicate; LFs = lithium iron silicate ($LiFeSi_2O_6$); m = minor.

DISCUSSION

There are two principal sources of thermal expansion of materials [8]. In most solids, the change of volume with temperature arises from the fact that constituent atoms vibrate about their equilibrium positions with an amplitude increasing with temperature. If the interatomic potentials were symmetrical, the average atomic spacings would be independent of the amplitude of vibration. Therefore, no thermal expansion would occur. However, this potential is not symmetrical, largely because when the atoms approach each other, a rapid increase in interatomic repulsive forces results. Therefore, the average separation increases with increasing amplitude, and the solid expands.

A second source of thermal expansion is the change in atomic arrangement of the material. In most crystalline solids, such changes are restricted to abrupt alterations in crystal form, although other effects, such as varying concentrations of vacancies, can contribute to the expansion. In the case of glasses, the atomic distribution function changes continuously, especially at sufficiently high temperatures, and contributes significantly to the observed expansion.

The expansion of a glass depends on the internal network structure, the arrangement of the individual building units and their bonding to each other. Douglas [9] argued that because of the nature of glass, configurational changes corresponding to changes in the distribution of bond length, bond angles, etc., will necessarily occur with a variation in temperature. However, Hummel [10] concluded that a change in bond angles seems to be the major factor in most cases of volume change due to thermal expansion.

Weyl and Marboe [5] 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.

In vitreous silica, the very low thermal expansivity at ordinary temperatures reveals strong forces and highly symmetrical short-range order. This is also expected in silica glass due to its open structure, with certain vibrational modes of the oxygen ions along the Si–Si axis [11–13]. The addition of the interstitial network-modifying ions causes a restoring force for transverse oxygen displacement which increases as the structure shrinks, thereby tending to give a positive expansion.

It is a generally accepted rule [14] that for most known glasses of varying composition, the coefficient of thermal expansion increases when the softening point decreases. Previous studies [15] revealed that the viscous properties of the iron-containing silica glasses are greatly influenced by the state of iron in the glass.

It was previously stated [16] that the thermal expansion could be governed by the bond strength and the bond character of the glass. The present results show that the single bond strength is not the only major factor controlling the thermal expansion data of the iron-containing glasses. To explain the fluctuation observed, the role played by iron in the internal structure and its concentration in such glasses are to be considered.

It is generally accepted [17] that both Fe^{3+} and Fe^{2+} ions are present in iron-containing glasses and that the ratio between them depends upon the composition of the glass and the melting condition. The Fe^{2+} ions tend to decrease with increasing iron concentration in the glass [1,3]. Kurkjian and Sigety [18] found that Fe^{3+} prefers octahedral sites in phosphate, and tetrahedral sites in silicate glasses. Other investigators [19] indicated that in silicate glasses, the ferric cations may occupy octahedral (FeO_6) and tetrahedral sites (FeO_4), while the ferrous cations occupy only octahedral sites. However, Bishay [20] concluded that the increase in the number of gaps in the glass structure, i.e., high concentration of non-bridging oxygen, will favour Fe^{2+} in network-forming positions as (FeO_4^{2-}). He also suggested that as the number of non-bridging oxygen atoms is greatly increased, the ferrous ions are oxidized to Fe^{3+}, a large percentage of which would favour network-forming positions as (FeO_4^{3+}).

In the glass composition investigated, it is believed that non-bridging oxygen atoms are present in appreciable amounts with such basic glasses of high alkali oxide content, the iron oxide tends to assume a lower coordination with the oxygen, and the bonding tends to be covalent [1]. In other words, the availability of non-bridging oxygen favours the increase of the oxidized species of the transition metal. Thus, it is expected that iron might exist as Fe^{3+} which is initiated more with high Fe_2O_3 content.

In the glasses investigated, in the low additives of iron, thermal expansion studies may suggest most of the Fe^{3+} entering in the network former positions. The rapid increase in the coefficient of expansion (α) on the Fe_2O_3/SiO_2 replacement of up to 2 mol% Fe_2O_3 (Fig. 2) may be explained on the basis that when Fe^{3+} ions form an FeO_4 unit, it is expected that Fe–O bonds of weaker character than Si–O bonds are introduced [21]. Consequently, high α values, and a rapid decrease in transformation and softening temperatures are expected. This might be due to the less rigid or loosely compact nature of the structure [22]. The alternative suggestion, that most of the Fe^{3+} ions enter as FeO_6 units, is unlikely. This is because when Fe^{3+} act as a modifier ion, it remains in the interstices and will not, in this case, alter the strength of the bonds between the connected tetrahedra. With an increasing Fe_2O_3-content of up to 4 mol% the cohesive force exerted by Fe^{3+} may come to play an important role, which may account for the lower α and the correspondingly higher T_g and T_s values of the glasses. However, in the range of 4–5 mol% Fe_2O_3 content, the thermal expansion of the glass tends to increase; meanwhile at higher iron oxide content the opposite results are obtained, which may be attributed to the variation of FeO_4/FeO_6 in the glass. Therefore, the fluctuation observed in the thermal expansion data of the glasses studied might be thought to be connected with the state of iron in the glass and the change in iron coordination with its concentration in the glass.

Although the parent glass contains 34 mol% Li_2O, i.e., it lies outside the miscibility gap, it is generally known that the addition of a third component can shift the immiscibility boundary [23].

The abnormal behaviour of the thermal expansion coefficient, transformation temperature and dilatometric softening point on Fe_2O_3 content (Fig. 2), may reveal that they are related not only to the state and coordination of the iron ions in glass, but also to the effect of iron ions on inducing phase separation in such glass compositions.

The development of phase separation and its type, whether it is metastable or unstable, is known to affect the thermal expansion behaviour [24].

In the crystalline state, the thermal expansion coefficient is quite different from that in the glassy state, it may increase, decrease, or remain practically unchanged during the crystallization process, depending upon the type and quantity of minerals which are formed during this process. A 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 [6]. 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 analyze the thermal expansion of glass-ceramics in relation to their constitution.

In general, the pyroxenes and lithium silicate phases have high positive values of thermal expansion. Diopside, which is considered to be of the pyroxene variety, has α values of $50–150 \times 10^{-7}\,^{\circ}C^{-1}$ (20–1000 °C) [25]. Meanwhile, lithium disilicate has a value of 110×10^{-7} [26] in the same range of temperature.

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

The present results reveal that the expansion coefficient of the glass-ceramics progressively increases with increasing iron oxide content (replacing silica) in the glasses investigated. This may be attributed to the formation of the alkali iron silicate phase ($LiFeSi_2O_6$) to the expense of the lithium silicate phase. There are no available thermal expansion data for this iron-containing silicate phase in the literature. The $LiFeSi_2O_6$ phase is a new variety of the clinopyroxene group [4]. This group of minerals are closely related in their crystallographic and other physical properties [27].

The present results also indicate that the thermal expansion coefficients of the crystalline material are temperature dependent. The α values of the glasses treated at a low temperature (700 °C) were higher than those obtained from the glasses treated at a higher temperature (i.e., 500 °C for 6 h, 850 °C for 10 h). This may be attributed to the enrichment of the residual glass (at a low temperature) with iron ions, since the iron-containing phase was noticeably developed at temperatures as high as 700 °C.

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