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Contribution of germanium dioxide to the thermal expansion characteristics of some borosilicate glasses and their corresponding glass-ceramics

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Abstract

The thermal expansion characteristics of some lithium aluminium germanium borosilicate glasses and their crystalline solids have been investigated. The base glass composition was modified by partial replacement of germanium dioxide instead of silica. In some cases, however, TiO_2 was also added to some selected glasses as a nucleation catalyst. Slight increase in the thermal expansion coefficient (α) values of the glasses and corresponding slight decrease in both transition (T_g) and softening (T_s) temperatures are detected by GeO_2/SiO_2 replacements, however, the reverse results were recorded by TiO_2 addition. The obtained data were correlated to the local structure changes induced by GeO_2 or TiO_2 and their contributions to the thermal expansion property of the glasses.

On the crystallization, the expansivity of the glasses was markedly changed. It was greatly affected by crystallization of GeO_2-containing phases and aluminosilicate solid solutions together with the TiO_2-containing phases formed. The results obtained were explained in relation to the nature, composition and concentration of all phases formed in the glass-ceramics including a residual glass matrix. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Germanium dioxide; Borosilicate glasses; Glass-ceramics

1. Introduction

The coefficient of thermal expansion (CTE) of different types of glass and glass-ceramic materials is often fundamental in determining their structure and fields of application [1]. Glass forming germanium dioxide has a higher linear coefficient of thermal expansion $75 \times 10^{-7}\ K^{-1}$ than either glass forming silicon or boron anhydride. The thermal expansion coefficient is the basis for the synthesis of glasses. Therefore, a high coefficient is of great importance to industrial applications that require high vacuum seals with metals such as brass or copper [2].

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 of the distribution of forces with increasing thermal vibrations [3]. 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

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[1,4]. 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 [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 coefficient close to those of useful metals are available [4,6]. The thermal expansion coefficient values of the glass-ceramics were found to be dependent on the type and relative proportions of the crystalline phases present as well as the nature of the remaining glassy phase [4].

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 coefficient [7,8].

The aim of the present work is to report the thermal expansion characteristics of GeO_2-containing borosilicate glasses and the corresponding glass-ceramics catalyzed by TiO_2 in order to detect the changes in the thermal expansion property that can result from the presence of GeO_2 and/or TiO_2 in the glasses and their crystalline solids.

2. Experimental

2.1. Glass composition

The composition of glasses is expressed by the following formula: $30\,Li_2O$–$10\,Al_2O_3$–$10\,B_2O_3$–$xGeO_2$–$(50-x)SiO_2$ mol%, where $x = 0$, 5, 10 and 15 mol%, were chosen in the present study. TiO_2 (5 g) was also added over 100 g of some selected glass oxide constituents.

2.2. Material preparation

The glasses were prepared from thoroughly mixed purified quartz and reagent grade Li_2CO_3, $Al(OH)_3$, H_3BO_3, GeO_2 and TiO_2. The weighed batches were thoroughly mixed and were melted in Pt–2% Rh crucible in an electric heated globar furnace at 1523–1573 K for 4 h with occasional stirring to ensure homogeneity. The homogeneous bubble-free melts were cast into rectangular rods of ($0.5\,cm \times 0.5\,cm$ cross-section and 1.5 cm length), and they were well annealed in a muffle furnace to minimize the strain of the glasses.

2.3. 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 773 K for 3 h and then at 973 K for 30 h.

X-ray diffractometry using a Ni filter and Cu radiation was used to identify the crystalline and solid solution phases formed.

2.4. Thermal expansion measurements

The coefficients of thermal expansion of the investigated samples were measured using Seiko 2200 automatic recording multiplier dilatometer with a heating rate of 278 K/min. The linear thermal expansion coefficient was automatically calculated using the general equation:

$$\alpha = \frac{\Delta L}{L}\frac{1}{\Delta T}$$

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

3. Results

The thermal expansion data of the investigated glasses and their respective crystalline solids including the variation of the expansion coefficient as a function of the GeO_2/SiO_2 replacements and TiO_2 addition are given in Table 1 and represented in Figs. 1–2 and 5–6.

3.1. Thermal expansion data of the glasses

The expansion curves of the glasses (Fig. 1) are generally similar to those characteristics of most

Table 1
Thermal expansion coefficient values of various investigated glasses and their crystalline solids[a]

Glass number	Composition	Phases developed	Expansion coefficients $\alpha \times 10^{-7}$ K^{-1}					T_g (K)	T_s (K)
			293–573°	293–673°	293–773°	293–873°	293–973°		
G_1	Base	Amorphous	90.6	–	–	–	–	761	808
C_1	Base	β-Eucryptite ss, α-L_2B (m), LS (m)	37.0	42.0	46.0	49.0	53.0	–	–
G_2	$5GeO_2/SiO_2$	Amorphous	91.3	–	–	–	–	746	784
C_2	$5GeO_2/SiO_2$	β-Eucryptite ss, LS, LB_2, $Li_{3.25}Al_{0.25}GeO_4$	7.0	12.0	15.0	21.0	25.0	–	–
G_3	$10GeO_2/SiO_2$	Amorphous	92.4	–	–	–	–	744	779
C_3	$10GeO_2/SiO_2$	β-Eucryptite ss, LS, $Al_2Ge_2O_7$, LB_2	29.0	30.0	33.0	36.0	41.0	–	–
G_4	$15GeO_2/SiO_2$	Amorphous	93.0	–	–	–	–	741	776
C_4	$15GeO_2/SiO_2$	β-Eucryptite ss, LS, $Li_{6.3}Al_{0.3}Ge_{1.7}O_7$, LB_2	31.0	33.0	36.0	38.0	42.0	–	–
G_5	Base+5TiO2	Amorphous	88.4	–	–	–	–	763	811
C_5	Base+5TiO2	β-Eucryptite ss, LS, $Li_2Ti_2O_4$, LB_2.	42.0	46.0	49.0	52.0	54.0	–	–
G_6	$10GeO_2/SiO_2 + 5TiO_2$	Amorphous	89.1	–	–	–	–	759	793
C_6	$10GeO_2/SiO_2 + 5TiO_2$	β-Eucryptite ss, LS, Li_2TiSiO_5, $Li_{2.875}Al_{0.375}GeO_4$, LB_4	40.0	45.0	49.0	51.0	52.0	–	–

[a] L_2B — lithium pyroborate, LS — lithium metasilicate, LB_2 — lithium diborate, LB_4 — lithium tetraborate, ss denotes the solid solution, m represents minor.

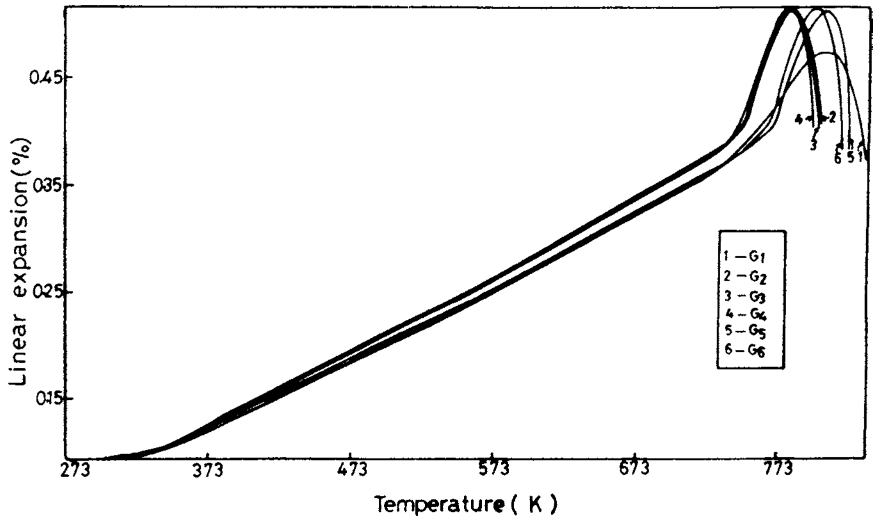

Fig. 1. Linear thermal expansion curves of GeO_2 and TiO_2 containing glasses.

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. Fig. 2 clearly indicates that the partial replacement of SiO_2 by GeO_2 increases the α-values of the glasses. Table 1 shows that the expansion coefficient of the base glass (G_1) is slightly increased by successive addition of GeO_2 in the expense of SiO_2 (G_2, G_3, G_4) and corresponding decrease in both glass transition (T_g) and dilatometric softening (T_s) temperatures. On the other hand, the addition of nucleator, i.e. TiO_2 to the glasses G_5 and G_6 decreases the thermal expansion coefficient of the glasses and increases their (T_g) and (T_s) values. Table 1 shows that the α-values of G_5 and G_6 (with TiO_2) are lower than those of G_1 and G_3 (free of TiO_2), respectively.

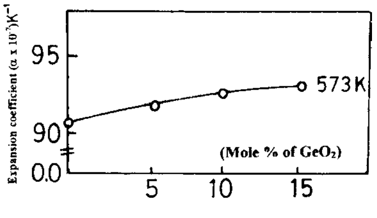

Fig. 2. Changes in expansion coefficients of glasses as a function of GeO_2/SiO_2 replacements.

3.2. Crystal phases developed in the glass-ceramics

The X-ray diffraction analysis (Fig. 3) revealed that β-eucryptite solid solution (ss) (major) together with minor amounts of lithium metasilicate and lithium

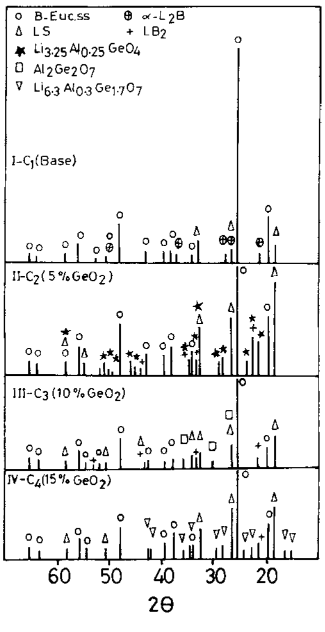

Fig. 3. XRD analysis of crystallized glasses of various GeO_2/SiO_2 replacements.

pyroborate phases, were formed in the base glass-ceramic (free of GeO_2 or TiO_2) pattern I. However, with 5 mol% GeO_2/SiO_2 replacement, i.e. C_2, lithium aluminium germanate solid solution ($Li_{3.25}Al_{0.25}GeO_4$) phase together with β-eucryptite ss, lithium metasilicate and lithium diborate phases were identified (pattern II).

At 10 mol% GeO_2/SiO_2 replacement, i.e. C_3, $Al_2Ge_2O_7$ phase together with β-eucryptite ss, lithium metasilicate and lithium diborate phases were detected (pattern III).

At higher GeO_2/SiO_2 replacement, C_4 (with 15 mol% GeO_2/SiO_2), lithium aluminium germanate-$Li_{6.3}Al_{0.3}Ge_{1.7}O_7$ was developed together with β-eucryptite ss, lithium metasilicate and lithium diborate phases (pattern IV).

On the other hand, lithium titanate ($Li_2Ti_2O_4$) in addition to β-eucryptite ss, lithium metasilicate and minor amount of lithium diborate phases were crystallized in the base glass containing 5% TiO_2 (C_5), Fig. 4, pattern II. However, lithium aluminium germanate ($Li_{2.875}Al_{0.375}GeO_4$), lithium titanium silicate (Li_2TiSiO_5) and lithium tetraborate were developed in addition to β-eucryptite ss and lithium metasilicate phases in crystalline glass containing 10% GeO_2/SiO_2 and 5% TiO_2 (C_6, Fig. 4, pattern IV).

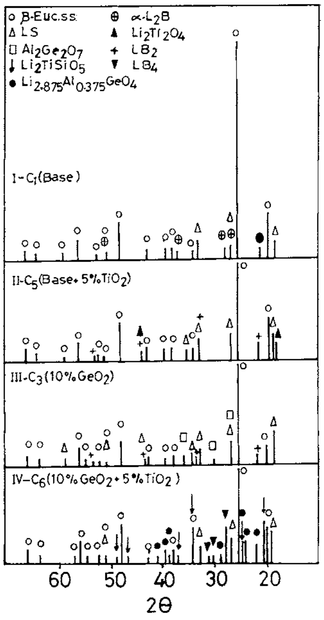

Fig. 4. XRD analysis of crystallized glasses containing TiO_2 as a nucleating agent.

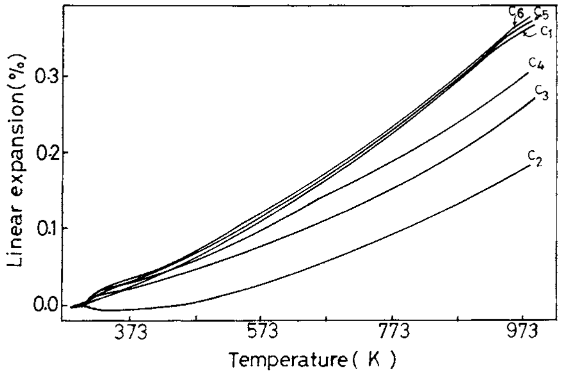

Fig. 5. Linear thermal expansion curves of GeO_2 and TiO_2-containing glass-ceramics.

3.3. Thermal expansion of the glass-ceramics

The resulting data revealed that the expansion coefficient of the crystalline products were generally much lower than those of the corresponding glasses (Table 1).

Considerable decrease of the α-values are detected by replacement of 5 mol% of SiO_2 by GeO_2. Table 1 and Figs. 5 and 6 indicated that the expansion coefficient of sample C_2 (5% GeO_2) is much lower than that of the base glass-ceramics. However, the α-values of samples C_3 and C_4 are higher than that of sample C_2, but they are still lower than that of the base glass-ceramic, i.e. C_1. With respect to the effect of TiO_2 on the expansion coefficients of the glass-ceramics, it is seen that the addition of TiO_2 increased the α-values of

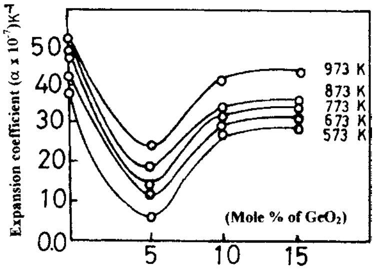

Fig. 6. Changes in expansion coefficients of glass-ceramics as a function of GeO_2/SiO_2 replacements.

TiO_2-containing samples. Table 1 clearly indicated that the α-values of C_5 and C_6 (with TiO_2) exhibit higher α-values than those of C_1 and C_3 (free of TiO_2), respectively.

4. Discussion

It is generally accepted that the thermal expansion of glass is not only a function of temperature but also sensitive to the structure of the glass, for example, degree of polymerization, type of structural units, the nature and contribution of the different cations, where they occupy forming or modifying positions in the glass network [5,9].

Germanate glasses are isostructural with silicates [2], they are studied for comparative purposes. Ge^{4+} and Si^{4+} cations carry the same charge and are, therefore, electrostatically equivalent. Because the Ge–O bond is weaker than the Si–O bond, an oxygen vacancy can be produced more easily near the Ge cation by trapping an electron [2,10].

Gulati and Helfinstine [11] showed that in silicate glasses, the coefficient of thermal expansion (CTE), as well as the density, increase with increasing GeO_2 content. This increase in GeO_2 leads to more Ge–O bonds in the glass structure, and this causes a weakening of the glass network structure [2]. Consequently, higher α-values and lower T_g and T_s temperatures could be expected.

On the other hand, the addition of TiO_2 to the glasses, i.e. G_5 and G_6 leads to a decrease of the α-values. This can be ascribed due to the role played by TiO_2 in the glass structure, which preferably exhibits a tetrahedral coordination (i.e. TiO_4) in the investigated glass composition [7,12,13]. This in turn will result into a firmer glass structure and leads to decrease the diffusion of different ions and ionic complexes. Therefore, a lower thermal expansion coefficient (α) of the glass and higher (T_g) and (T_s) values could be expected, as compared with the glasses free of TiO_2.

The thermal expansion property of the crystalline solids is quite different from that of the parent glasses. The thermal expansion coefficient (α) of the glass-ceramics is a function of the thermal expansion coefficients and elastic properties of all crystalline phases present including residual glass. The contribution of the residual glassy phase, whose composition is altered from that of the parent glass, must be taken into account [7,8].

An extremely wide range of thermal expansion coefficients is covered by the different crystal types and the development of these phases in appropriate proportions form the basis of the production of glass ceramics with controlled thermal expansion coefficients [1,7].

The crystallization of lithium aluminoborosilicate glasses generally produces crystal phases such as β-eucryptite with much lower expansion coefficient [1,14] than those of the parent glasses. The contribution of a particular crystal phase to the thermal expansion of a glass ceramic may be also modified if the crystal enters into solid solution with another phase. β-Eucryptite has high negative expansion of $-86 \times 10^{-7}\ K^{-1}$ (293–973 K) and $-64 \times 10^{-7}\ K^{-1}$ (293–1273 K) [1,7]. The expansion coefficient of lithium diborate has a high positive value of $138 \times 10^{-7}\ K^{-1}$ (573–873 K) [15]. Lithium titanium silicate (Li_2TiSiO_5) also has a relatively high positive thermal expansion coefficient ($76 \times 10^{-7}\ K^{-1}$, 293–1273 K) [16]. There is no detailed data available in the literature about the thermal expansion coefficients of GeO_2-containing phases.

Darwish [17] pointed out that different varieties of germanium containing phases were developed from crystallization of lithium aluminium germanium borosilicate glasses.

The present results revealed that an abrupt decrease in the α-values of the crystalline solids caused by addition of 5% GeO_2 instead of SiO_2 (C_2) may be attributed to the formation of $Li_{3.25}Al_{0.25}GeO_4$ solid solution phase, which is isostructurally with the β-eucryptite phase of low thermal expansion coefficient property. Tien and Hummel [18] pointed out that the substitution of Ge^{4+} for Si^{4+} produced no significant difference in the thermal expansion coefficient in the α- and β-eucryptite phase. Also, the lower α-values given by sample C_3 as compared with that of the parent sample C_1 may be attributed to the formation of $Al_2Ge_2O_7$ phase

The decrease of the α-values given by the glass-ceramics of 15 mol% GeO_2 (i.e. C_4) may be ascribed to the crystallization of the $Li_{6.3}Al_{0.3}Ge_{1.7}O_7$ phase in the sample.

The formation of $Li_{2.875}Al_{0.375}GeO_4$ in sample C_6 (with GeO_2) may explain the lower α-value as compared with that obtained from the sample C_5 (free of GeO_2).

With respect to the effect of addition of TiO_2 in the glasses, it was known that, TiO_2 influenced the type of the resulting phases and their transformation temperatures [7,12,13]. Therefore, the increase in α-values of the glass-ceramic C_5 (base + TiO_2) as compared with that free of TiO_2 may be attributed to the formation of lithium titanate and lithium diborate instead of minor amount of lithium pyroborate. Also, the increase in the α-values of sample C_6 (with GeO_2 and TiO_2) as compared with that of sample C_3 (free of TiO_2) may be ascribed to the formation of highly expanding lithium titanium silicate (Li_2TiSiO_5) [16] and lithium tetraborate at the expense of lithium diborate phase.

5. Conclusions

The thermal expansion properties of some lithium aluminium germanium borosilicate glasses and corresponding glass-ceramics nucleated by TiO_2 have been investigated.

The α-values of the investigated glasses were generally increased by GeO_2/SiO_2 replacements, while both (T_g) and (T_s) decreased. However, the reverse results were reported by TiO_2 addition in the glasses.

The thermal expansion coefficients were markedly changed by conversion of the glasses into glass-ceramic materials. The crystallization of germanium-containing phases was generally affected the thermal expansivity of the glass-ceramics. An abrupt decrease of the α-values was markedly observed by the formation of $Li_{3.25}Al_{0.25}GeO_4$ phase in the glass-ceramics. However, the formation of lithium titanate or lithium titanium silicate phases considerably increased the expansion coefficient of TiO_2-containing glass-ceramics.

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