THERMAL EXPANSION OF HIGH LEAD BORATE GLASSES AND THE BORIC OXIDE ANOMALY

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ABSTRACT

The thermal expansion of some binary high lead oxide–boric oxide glasses and glasses derived from them by replacements were measured. The thermal expansion coefficient, α, was calculated at successive temperatures up to the dilatometric softening temperature. The experimental results and the anomalies observed were discussed on the basis of the different views concerning the changes in the boron coordination with composition. The differing effects of the introduced oxides were related to the ionic sizes of the cations and the ease of movement or fluidity of the internal structural units.

INTRODUCTION

Glasses containing lead oxide have long working ranges and high refractive indices which make them useful for lead crystal, optical glass and hand-formed art ware. Lead glasses effectively shield high-energy radiation and are therefore used commercially for radiation windows, fluorescent-lamp envelopes, and television bulbs. Low-melting solder glasses and frit or decorative enamels are usually based upon low-melting lead compositions. These various applications necessitate that the properties of such glasses are thoroughly investigated in relation to composition and internal structure.

The thermal expansion of a glass is primarily related to the internal structure because of its sensitivity to the number and sizes of building unit aggregates. It is one of the few techniques providing some insight as to the manner in which the molecular units link to one another.

In alkali silicates a sudden increase in expansion appears at 12 mole % alkali oxide, suggesting a fundamental change in structure [1–3]. In germanates it occurs at 1% and does not necessarily indicate that the network is modified in the way proposed for silicates [4]. Borates exhibit altogether different behaviour according to the coordination of boron [5].

In previous publications from our laboratory, the thermal expansion of cabal glasses [6], and glasses containing high lead silicate glasses [7] were investigated. The change in the coefficient of thermal expansion with chemi-

cal composition was understood and realized by considering the changes in the bond strengths, ionic sizes and the ease of movement of the building units. No abrupt change in the thermal expansion was found in the glass compositions studied.

Glass preparation

Glass batches were prepared from pure grade raw materials. Lead oxide was introduced as red lead (minimum Pb_3O_4). Boric oxide was added in the form of orthoboric acid (H_3BO_3) while alkali and alkaline earth oxides were introduced as the respective carbonates except ZnO which was added as such.

Mixed glass batches were melted in platinum/2% rhodium crucibles in a muffle electric furnace at temperatures of 1000–1200°C according to the chemical composition. Melting was continued for almost four hours with stirring a few times to produce satisfactory homogeneous glass. The melt was cast as rods of the required dimensions and properly annealed to room temperature.

For thermal expansion measurements a rod specimen approximately $0.5 \times 0.5 \times 5$ cm was required. The ends and the whole bulk of the glass were ground flat and parallel. The glass sample dimension was measured with a high precision micrometer which was read to three decimal places.

Thermal expansion measurements

The annealed specimen was inserted into the quartz tube dilatometer and its dial gauge was set at zero; the initial temperature was read and recorded. The cumulative expansions were obtained every 25°C. The furnace of the dilatometer was adjusted to obtain a periodic continuous increase of about 15–20°C per minute interval. Data were obtained for each glass composition specimen from room temperature to the dilatometric softening point of the glass. At least two measurements were made on each specimen and the results were found to be fairly reproducible. The apparatus was calibrated against samples of Corning glass-ceramics code 9606 and 9608.

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

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

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

RESULTS

Results of the present study are shown in Figs. 1–9. During the first part of the cumulative expansion vs. temperature curve, the relation was linear up to the dilatometric temperature of the glass.

Figures 1 and 2 show a plot of thermal expansion vs. temperature of a series of lead oxide–boric oxide glasses. From these curves it can be seen that the dilatometric softening temperature decreases with the increase of PbO content in the glass. Replacing 2, 5 or 10 parts of PbO by lithia or magnesia increases the dilatometric softening temperature of the glass (Figs. 3 and 4) while the replacement of boric oxide by alumina decreases the softening temperature (Fig. 5). Figure 6 shows a plot of linear coefficient of thermal expansion (α) against chemical composition of binary PbO–B_2O_3 glasses at various temperatures. From the curve it is seen that at all temperatures the coefficient of thermal expansion progressively increases with the increase of PbO content but with two inflections or shallow minima. The first inflection lies at the glass composition PbO 70%, B_2O_3 30% and the second inflection has a maximum at the glass composition PbO 85%, B_2O_3
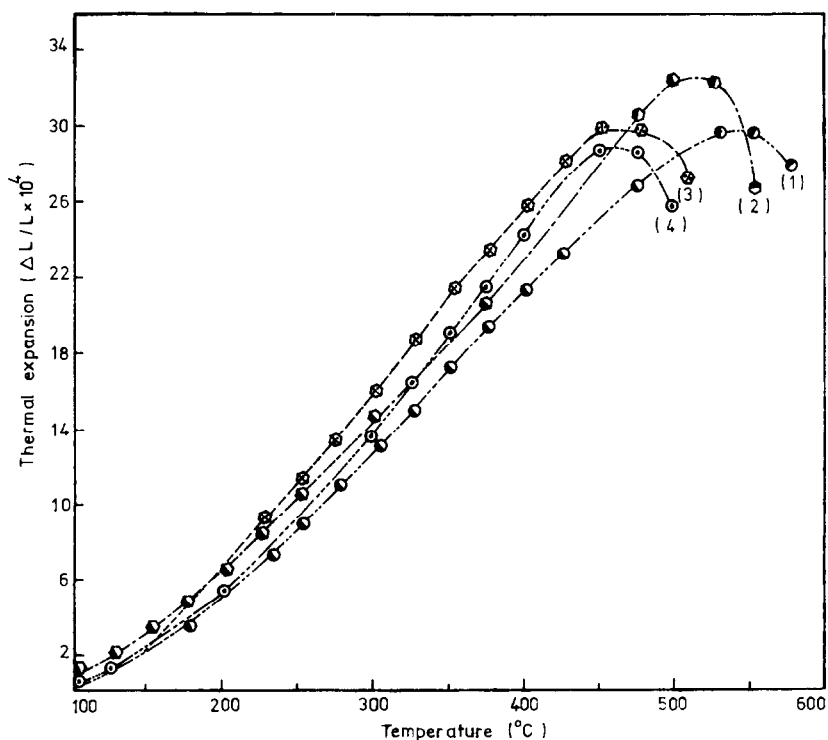

Fig. 1. Thermal expansion curves of $PbO \cdot B_2O_3$ glasses. (1), 55% $PbO \cdot 45\%$ B_2O_3; (2), 60% $PbO \cdot 40\%$ B_2O_3; (3), 65% $PbO \cdot 35\%$ B_2O_3; (4), 70% $PbO \cdot 30\%$ B_2O_3.
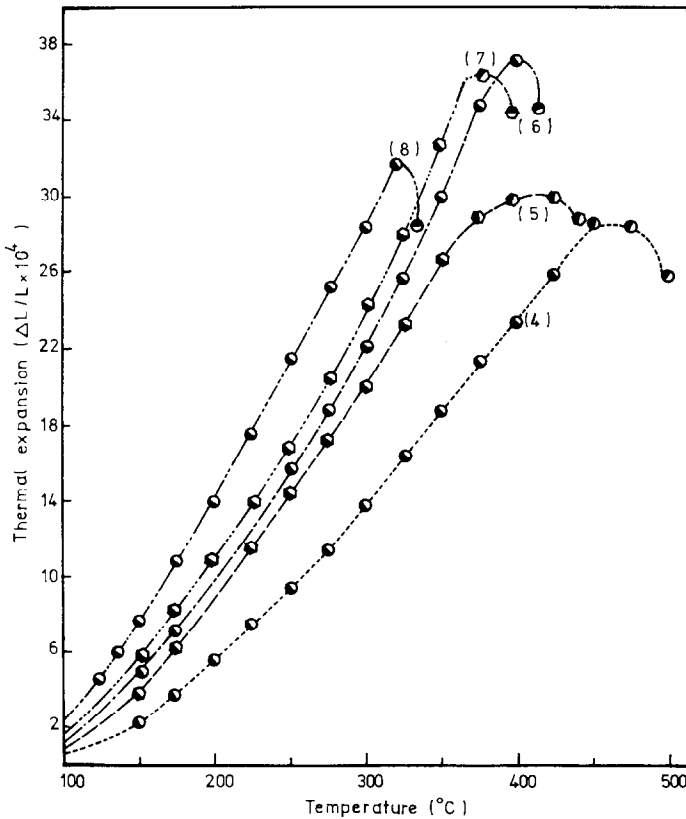
Fig. 2. Thermal expansion curves of PbO·B₂O₃ glasses. (4), 70% PbO·30% B₂O₃; (5), 75% PbO·25% B₂O₃; (6), 80% PbO·20% B₂O₃; (7), 85% PbO·15% B₂O₃; (8), 90% PbO·10% B₂O₃.

15%. At higher concentrations of PbO (80% or more) the second minimum cannot be followed at high temperatures owing to the lower softening temperatures of such glasses.

Our experimental results indicate that the thermal expansion coefficients of the lead borate glasses are temperature dependent.

Figures 7 and 8 show the effect of replacing 2, 5 or 10% of PbO by Li_2O or MgO on the thermal expansion coefficient of lead borate glasses. From these curves, it is seen that the thermal expansion coefficient decreases with 2% replacement and then progressively increases with further replacements but does not exceed the initial values. The replacement of 2% of B_2O_3 by Al_2O_3 decreases the thermal expansion coefficient but with further substitution of 5 or 10%, the thermal expansion coefficient again increases (Fig. 9).

Table 1 gives the calculated thermal expansion coefficients of all the glass samples in the range 100–300°C and the data are reproducible and comparable with the published data on related chemical compositions.
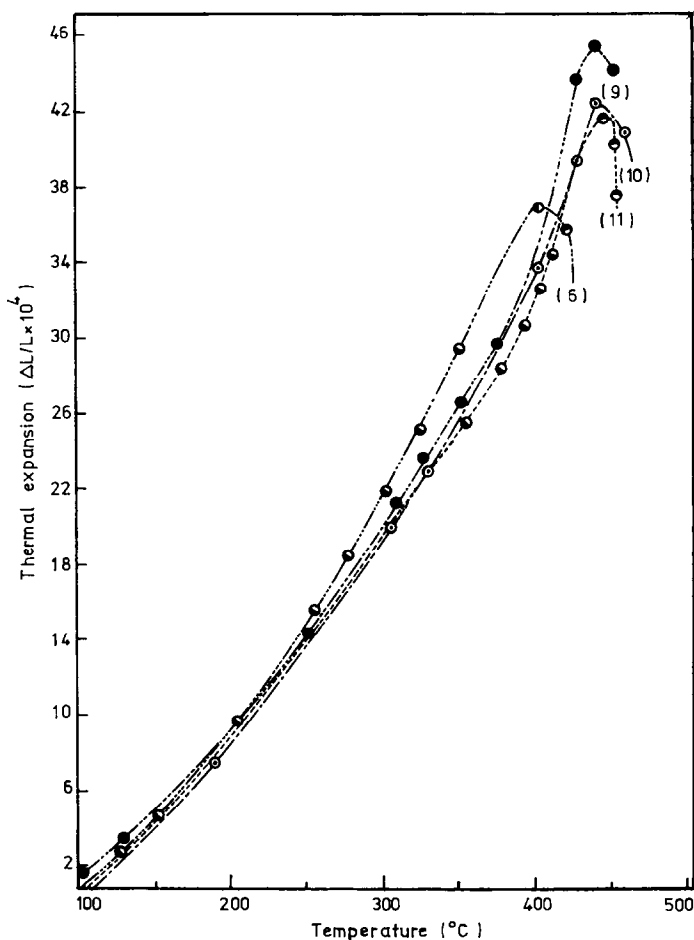
Fig. 3. Thermal expansion curves of lead borate glasses containing Li_2O. (6), 80% $PbO \cdot 20\%$ $B_2O_3 \cdot 0\%$ Li_2O; (9), 78% $PbO \cdot 20\%$ $B_2O_3 \cdot 2\%$ Li_2O; (10), 75% $PbO \cdot 20\%$ $B_2O_3 \cdot 5\%$ Li_2O; (11), 70% $PbO \cdot 20\%$ $B_2O_3 \cdot 10\%$ Li_2O.

DISCUSSIONS

Although for practical purposes the thermal expansion is one of the more important properties of a glass, there is no satisfactory description of the effect at a microscopic level. The main reason for this is the complexity of the subject. A complete calculation of the thermal expansion requires not only a knowledge of the vibrational density of states, but also an understanding of the way in which each vibrational mode changes with pressure and temperature.

Normal expansion in solids, including glass, is described as being due to the increasing amplitude of atomic vibrations of the constituents [8]. From lattice energy considerations the ionic vibrations are anharmonic and
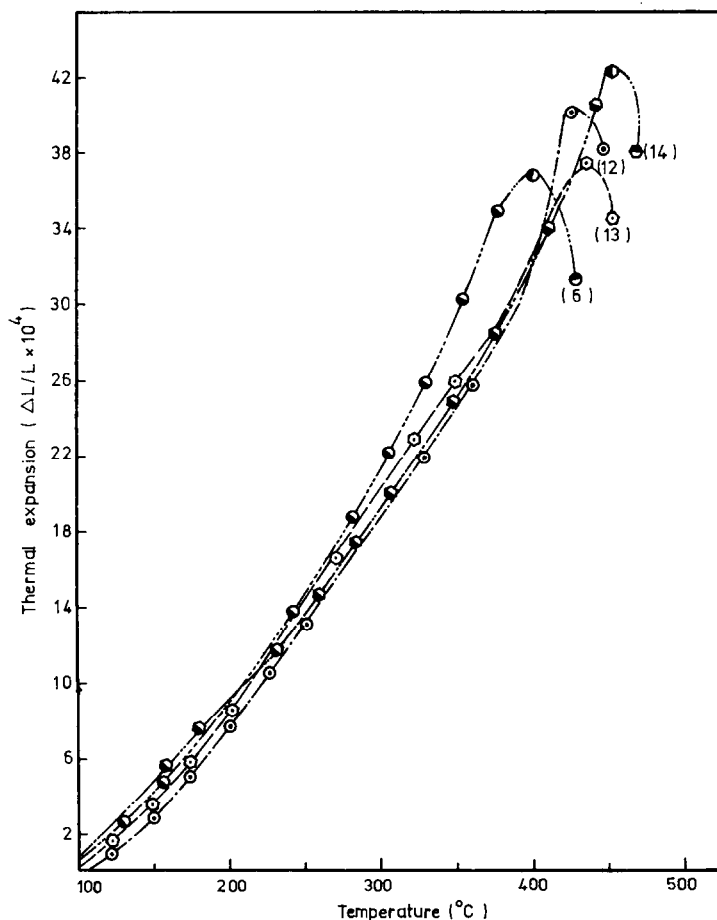
Fig. 4. Thermal expansion curves of lead borate glasses containing MgO. (6), 80% PbO·20% B_2O_3·0% MgO; (12), 78% PbO·20% B_2O_3·2% MgO; (13), 75% PbO·20% B_2O_3·5% MgO; (14), 70% PbO·20% B_2O_3·10% MgO.

as a result, with increasing amplitude of vibration, the interionic distance increases [9]. The ions vibrate independently of each other.

The relatively small thermal expansion coefficient of a given annealed glass (normally from 0 to 150×10^{-7} below viscosity $10^{4.5}$ P) is most likely due to cation vibrational effects with a relatively small contribution from rotational effects caused by non-directional bonds associated with modifying cations [10]. Also, the relatively sudden decrease in the expansion coefficient from the strain point to annealing point region is coincident with the onset of longer relaxation times for various transport phenomena for cations and polyanionic aggregates.

Although the changes in boron coordination from three to four is known to significantly alter some properties of glass (e.g. softening point [11,12] and
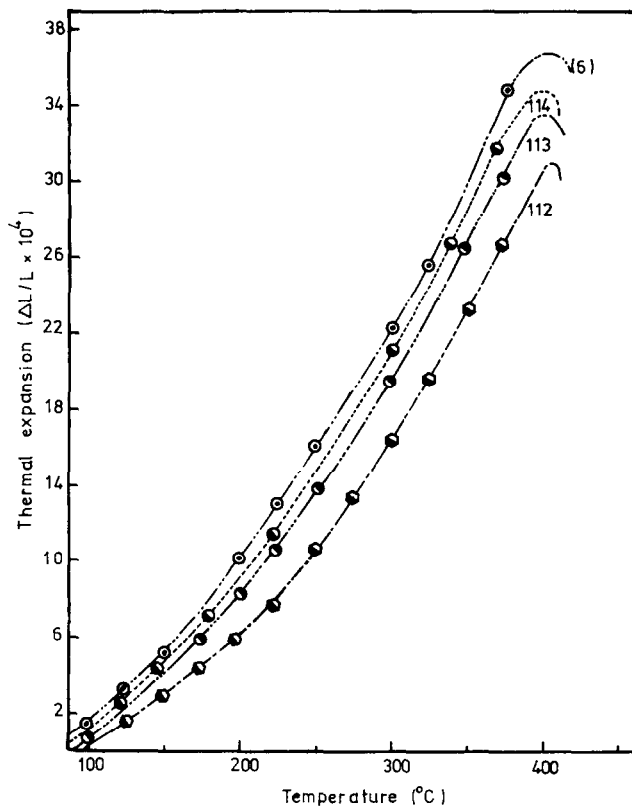
Fig. 5. Thermal expansion curves of lead borate glasses containing Al_2O_3. (6), 80% $PbO \cdot 20\%$ $B_2O_3 \cdot 0\%$ Al_2O_3; (112), 80% $PbO \cdot 18\%$ $B_2O_3 \cdot 2\%$ Al_2O_3; (113), 80% $PbO \cdot 15\%$ $B_2O_3 \cdot 5\%$ Al_2O_3; (114), 80% $PbO \cdot 10\%$ $B_2O_3 \cdot 10\%$ Al_2O_3.

IR spectra [13], it has only a small effect on other properties (e.g. density and refractive index [14,15].

Experimental results of the present study indicate that the thermal expansion coefficient falls into the first category.

To account for such variations or "anomalies" observed in some of the property vs. composition relations, it is helpful to introduce the possible change in the network structure of the glasses with composition.

The structure of high lead borate glasses

Although lead oxide is not considered as a glass-former, glasses containing as high as 90 wt.% PbO have been easily prepared in binary $PbO-B_2O_3$ systems.

Early investigators of high-lead glasses assumed that [16,17] the stability of such glasses is due to the high polarizability of the Pb^{2+} ion, which has an outer shell of eighteen electrons. The high cation polarizability results in the
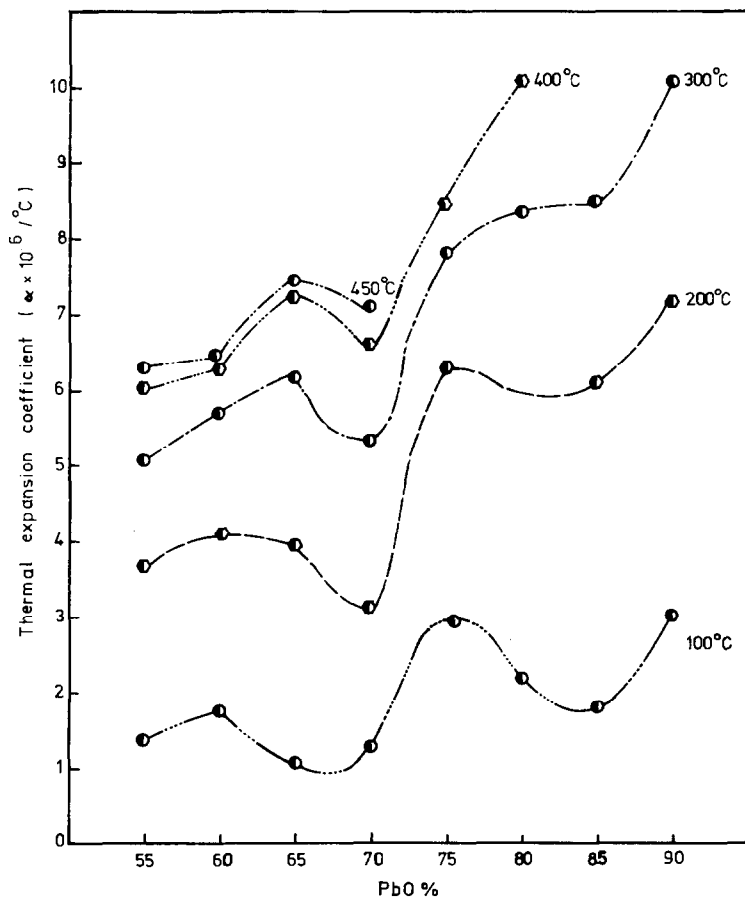
Fig. 6. Thermal expansion coefficients of PbO·B$_2$O$_3$ glasses.

Pb–O bond being more directional than, for example, the Na–O bond. It is believed that on crystallization it will be more difficult to rearrange SiO$_4$ or BO$_3$ groups linked together through these directed bonds than would be the case if the bonds had no directional character. Fajans and Kreidl [16] illustrate the asymmetrical character of the bonding between a Pb^{2+} ion and surrounding oxygen anions by referring to the structure of PbO. The lead ion is considerably nearer to four of the surrounding oxygens than to the other four and is more strongly bonded to the nearer oxygens. Stanworth, on the other hand, believes [18], in a manner consistent with Bair's conclusion [19], that the lead atoms are bonded to only two oxygens and may be regarded as taking part in the glass network. Such a structure is obviously a very open one and further PbO (over the orthosilicate) might be added by coordinating more oxygens around the lead atoms in the network and allowing the excess lead ions to find suitable places in the holes of the network.
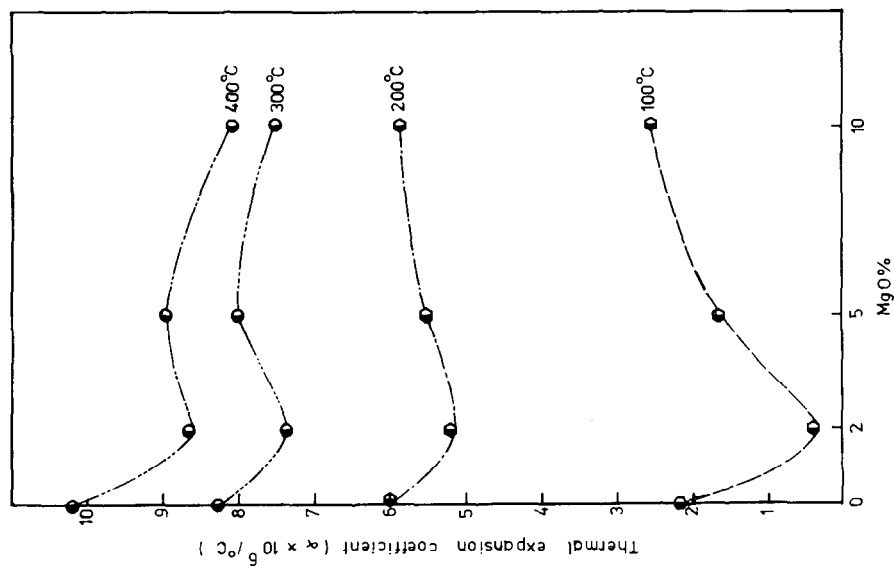
Fig. 8. Thermal expansion coefficients of lead borate glasses containing MgO.
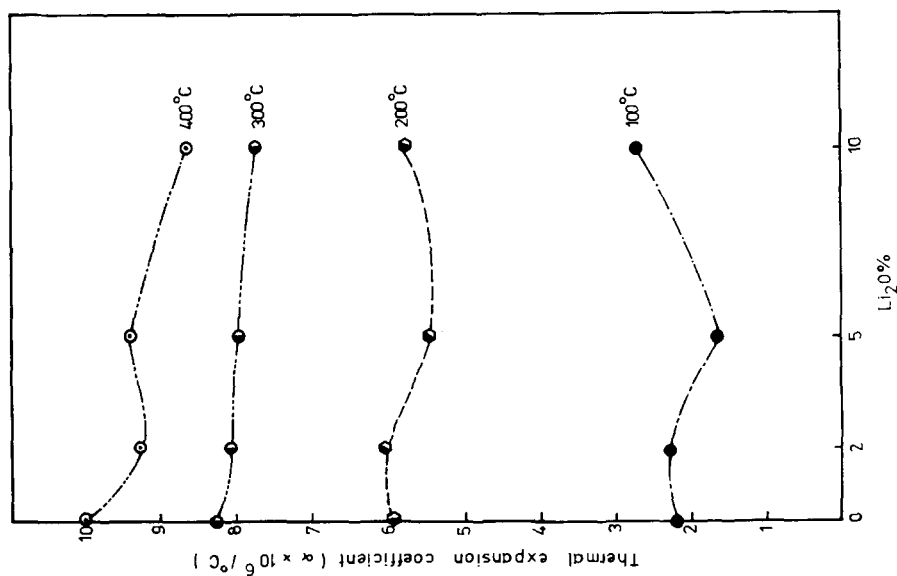

Fig. 7. Thermal expansion coefficients of lead borate glasses containing Li₂O.
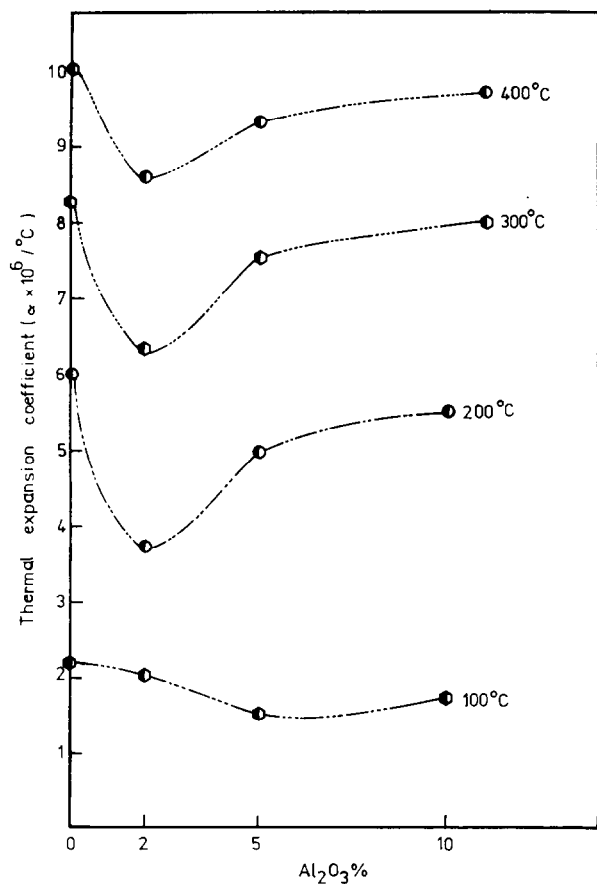
Fig. 9. Thermal expansion coefficients of lead borate glasses containing Al_2O_3.

Nuclear magnetic resonance studies [20] on lead borate glasses have indicated that all or most of the lead is present as Pb^{2+} ions in glasses containing less than perhaps 20–30 mole% PbO. In glasses containing larger amounts of PbO, some of the lead atoms apparently enter the network and bond to oxygen configurations. The fraction of boron atoms that are four-coordinated (N_4) in the glass was observed to increase from approximately 0.25 to a maximum of about 0.52 over the composition range of approximately 20–50 mole% PbO. Further addition of PbO produced a decrease in N_4 to about 0.22 at 75 mole% PbO.

The nature of the structural units present in lead borate glasses has not been considered in detail in accordance with the previous assumption introduced by Krogh-Moe regarding alkali borate glasses [21]. The existence of groups such as boroxol, triborate, pentaborate or diborate have not had their existence confirmed in lead borate glasses.

Our results can be understood when it is considered that the thermal

TABLE 1

Thermal expansion coefficients of lead borate glasses in the temperature range 100–300°C

Glass no.	Composition (wt.%)			$\alpha \times 10^6$
	PbO	B_2O_3		
1	55	45		6.7
2	60	40		7.3
3	65	35		8.2
4	70	30		6.9
5	75	25		9.3
6	80	20		9.4
7	85	15		11.7
8	90	10		13.5
			Li_2O	
9	78	20	2	10.2
10	75	20	5	11.1
11	70	20	10	9.6
			MgO	
12	78	20	2	10.2
13	75	20	5	9.9
14	70	20	10	9.4
			Al_2O_3	
112	80	18	2	8.1
113	80	15	5	9.8
114	80	10	10	10.7

expansion may be related to the internal structure and to the number and sizes of the anionic aggregates. The thermal expansion of an oxide network would be expected to increase as the network becomes more open [22] or exhibit a less rigid and loose structure.

With the first additions of PbO to B_2O_3, the boron coordination is expected to change from three to four by the additional oxygen with the lead occupying interstitial positions. This change is associated with a change in bonding character from 2-dimensional to 3-dimensional with an attendant increase in the tightness of the structure initiating a decrease in the expansion coefficient. There is competition between two processes, the formation of boron in tetrahedral coordination tending to decrease the expansion coefficient, and the introduction of modifying cations, tending to increase it. It was shown that [23] the larger the size of the cation, the larger its effect on the expansion coefficient. The effect of the modifying cations is dominating and an increase in the thermal expansion coefficient is observed. With a further increase in PbO content, a possibility arises that a third factor must be taken into consideration, namely, the creation of non-bridging oxygens. At low concentrations of PbO, the number of non-bridging oxygen ions is too small to disturb the coherence of the network to a measurable degree. It

is generally believed [24] that properties that are sensitive to the occurrence of non-bridging oxygen ions (or to the degree of coherence of the network) may show an "anomalous" behaviour. The combined effect of increasing the number of non-bridging oxygen ions and the possible decrease of the boron in tetrahedral coordination might explain the further progressive increase in the thermal expansion coefficient with high PbO content.

It is equally important to mention that the positions of the observed minima (or so-called anomaly behaviour) can be related to the possible presence of two types of BO_3 groups which are observed in NMR spectra of alkali borate glasses [25–27]. However, the detailed existence of such groups in lead glasses has not yet been ascertained.

It is generally accepted that [7,18] the magnitude of the binding energy increases with the valencies and decreases with the size of the atoms. It is therefore expected that glasses containing PbO would have lower dilatometric softening temperatures due to the ease of movement or fluidity of the atomic constituents [28,29]. On the same grounds, the coefficient of thermal expansion is assumed [30] to increase with the increase in the percentage ionic character of the glass.

The relative effect of lithia or magnesia can be understood when it is realized that replacing Pb^{2+} (ionic size 1.2 Å) by Li^+ or Mg^{2+} (ionic sizes 0.60 and 0.65 Å, respectively) will be expected to increase to dilatometric softening temperature due to the relative compactness of the network structure. The effect of MgO is seen to be higher as it is expected that MgO_4 groups are formed in extremely basic lead glasses [31]. The role of Al^{3+} (ionic size 0.50 Å and single bond strength with oxygen of 60 cal mole^{-1}) replacing B^{3+} (ionic size 0.2 Å and single bond strength with oxygen of about 100 cal mole^{-1}) is quite different. The ability of alumina, as an intermediate oxide to form AlO_4 groups in B_2O_3, or to be housed in octahedral coordination in the glass interstices, is known. Our results indicate that Al^{3+} is preferably housed in such glasses in interstitial positions and this explains the slight progressive decrease in the dilatometric softening temperature.

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