THERMAL EXPANSION OF HIGH LEAD SILICATE GLASSES IN RELATION TO STRUCTURE

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ABSTRACT

The thermal expansion of some binary and ternary high lead silicate glasses was measured from room temperature to above the softening temperature. The expansion curves for all the glasses showed similar characteristics. The increase of lead oxide content increased the thermal coefficient of expansion but to a lesser extent than the alkaline fluxes. The various proposed mechanisms of thermal expansion were advanced and the experimental results could be explained by considering the bond strengths and ionic sizes of the cations. The possible effects of compactness and phase separation of the structure were also examined.

INTRODUCTION

The thermal expansion of a glass determines the range of materials to which it can be safely sealed. It also affects the ability of the glass to survive thermal shock or cycling. With a few exceptions, the volume of all solid bodies increases with increasing temperature if the external pressure on the body is constant [1]. 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 vibrations [2].

A solid is considered as an array of oscillating masses. However, one must not equate thermal expansion to the increase in amplitude of vibration of the atoms as the temperature increases [3]. The total expansion is only ~ 8% of the maximum amplitude of vibration. The interatomic spacing, and therefore the dimensions of a solid, change with temperature only because the oscillations are not harmonic.

There are two forces acting on an atom or ion in a particular solid: an electrostatic attractive force which increases as the inverse square of their separation, and an additional repulsive force due to an interaction between the electrons in the closed shells of the ions. The present experimental investigation was conducted to gain insight into the effect of the structure on the thermal expansion behaviour of high lead silicate glasses.

EXPERIMENTAL

Glass preparation

The glasses studied had compositions in the range 1 SiO_2, 0.5 PbO and 1 SiO_2, 1.52 PbO. They were obtained by combining glass oxides that gave desirable melting and forming characteristics. Lead oxide was introduced as red lead (minimum Pb_3O_4). The silica source was purified and pulverized Dutch Silver sand of the highest grade available, with the minimum amount of iron contamination. Boric oxide was introduced as orthoboric acid, H_3BO_3. Magnesia, lime and strontium oxide were introduced as the respective carbonates; ZnO was added as such. Batches were weighed on a Mettler sensitive balance. Mixing of the batch was accomplished until the batch looked uniform pink, showing good dispersion of the red lead. Melting was carried out in platinum 2% rhodium crucibles in a SiC glober-heated electric furnace at temperatures of $1350 \pm 20°C$ for almost 4 h until the glass was well melted. The melts were stirred a few times during melting.

For thermal expansion measurements, a specimen 1×5–6 cm was required. The glass was cast in stainless steel molds and was properly annealed at the appropriate temperature for each composition. The ends and the whole bulk of the glass were ground flat and parallel. The sample thickness was measured with a high precision micrometer which was read to three decimal places.

Thermal expansion measurements

The specimen was loaded into the quartz tube dilatometer and its dial gauge was set at zero, initial temperature was read and recorded. The cumulative expansions were obtained every 25°C. The furnace of the dilatometer was raised periodically to maintain about a 25–30°C temperature rise per 5 min interval. Data were obtained for each specimen from room temperature to the softening point of the glass. At least two measurements were made on each specimen within 2%. The quartz dilatometer was calibrated against samples of Corning glass-ceramics code 9606 and 9608. The linear coefficient of thermal expansion was then calculated using the equation

$$\alpha = \frac{\text{Increase in length } (\Delta L)}{\text{Original length of specimen } (L) \times \text{increase in temp.} (\Delta T)} + 0.54 \times 10^{-6}$$

The last term in this equation is the correction factor for the expansion of the quartz tube.

RESULTS

The expansion curves for all the glass compositions (Figs. 1–6) showed similar characteristics. During the first 25–50°C of heating the expansion of the specimen was quite small. This was probably due to the time it took the heat to penetrate through the quartz·tube and the start of specimen heating. From this point on the temperature versus cumulative expansion curve was quite linear up to between 450 and 600°C, depending on the particular composition. When the curve changed from linearity the trend was to a sharply increased expansion rate. This change from linearity is referred to as the transformation range of the glass, and is a well documented phenomenon in various glasses [4]. The transformation regions for the glasses in this study were between 35 and 75°C. After this period, the expansion of the rod seemed to cease for a period of about 25°C and then started to drop rapidly, indicating that the specimen had reached its softening temperature.

Figures (7–12) show a plot of linear coefficient of thermal expansion (α) against chemical compositions of glasses at various temperatures. In binary lead oxide–silica glasses the coefficient at low temperatures (100 and 200°C) decreases with the increase of lead oxide content, and at higher temperatures (from 300 to 500°C) the coefficient increases with the increase of lead oxide. With the addition of boric oxide replacing silica, α increases and the transformation temperature continuously decreases. With the introduction of
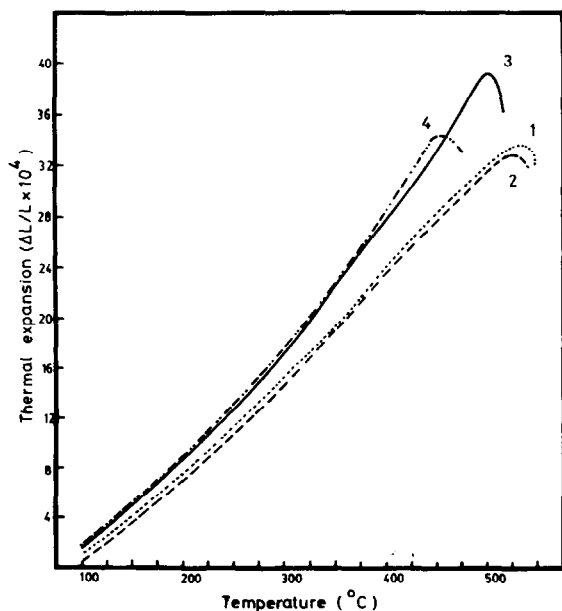

Fig. 1. Thermal expansion curves of PbO–SiO$_2$ glasses. (1) 70% PbO, 30% SiO$_2$; (2) 75% PbO, 25% SiO$_2$; (3) 80% PbO, 20% SiO$_2$; (4) 85% PbO, 15% SiO$_2$.
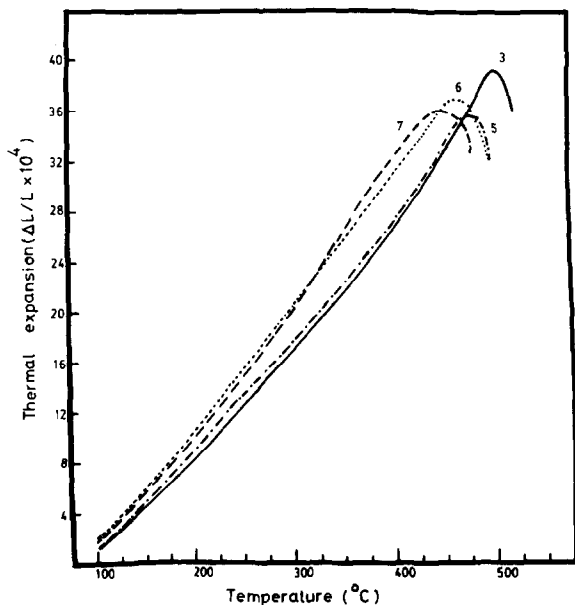
Fig. 2. Thermal expansion curves of lead silicate glasses containing B_2O_3. (3) 80% PbO, 20% SiO_2, 0% B_2O_3; (5) 80% PbO, 19% SiO_2, 1% B_2O_3; (6) 80% PbO, 18% SiO_2, 2% B_2O_3; (7) 80% PbO, 15% SiO_2, 5% B_2O_3.
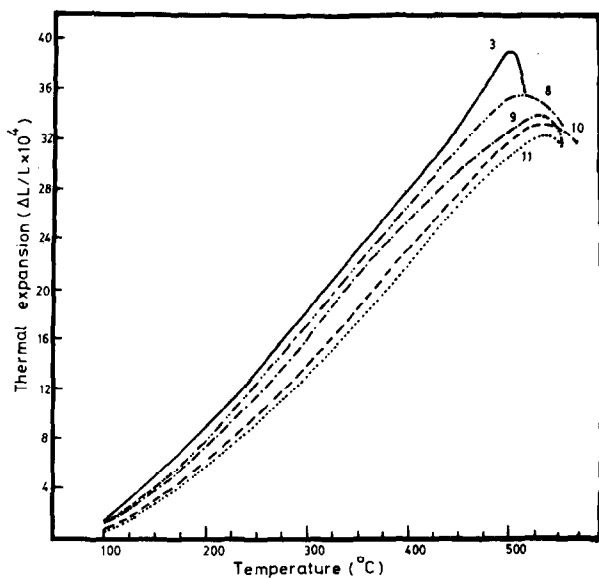

Fig. 3. Thermal expansion curves of lead silicate glasses containing CaO. (3) 80% PbO, 20% SiO_2, 0% CaO; (8) 79% PbO, 20% SiO_2, 1% CaO; (9) 78% PbO, 20% SiO_2, 2% CaO; (10) 75% PbO, 20% SiO_2, 5% CaO; (11) 70% PbO, 20% SiO_2, 10% CaO.
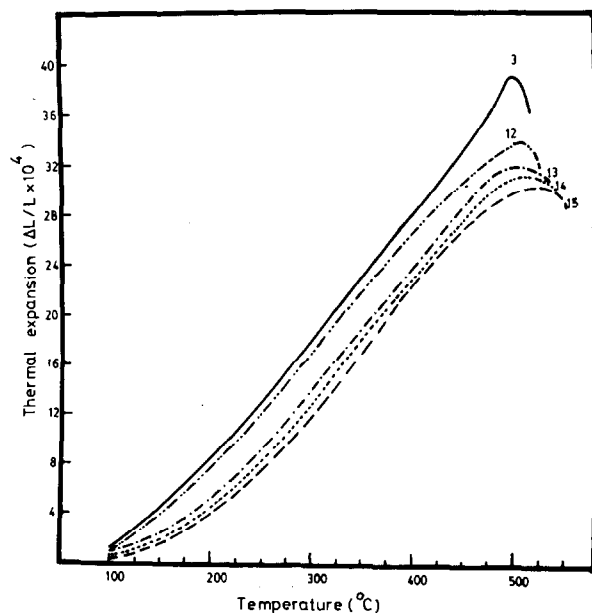
Fig. 4. Thermal expansion curves of lead silicate glasses containing SrO. (3) 80% PbO, 20% SiO_2, 0% SrO; (12) 79% PbO, 20% SiO_2, 1% SrO; (13) 78% PbO, 20% SiO_2, 2% SrO; (14) 75% PbO, 20% SiO_2, 5% SrO; (15) 70% PbO, 20% SiO_2, 10% SrO.
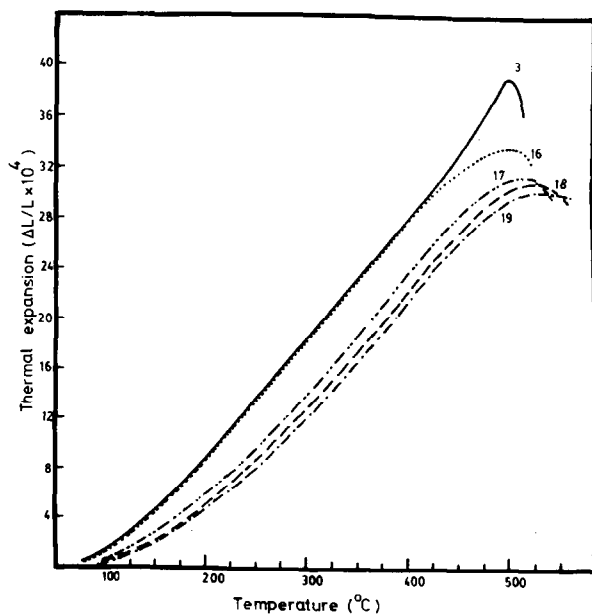

Fig. 5. Thermal expansion curves of lead silicate glasses containing ZnO. (3) 80% PbO, 20% SiO_2, 0% ZnO; (16) 79% PbO, 20% SiO_2, 1% ZnO; (17) 78% PbO, 20% SiO_2, 2% ZnO; (18) 75% PbO, 20% SiO_2, 5% ZnO; (19) 70% PbO, 20% SiO_2, 10% ZnO.
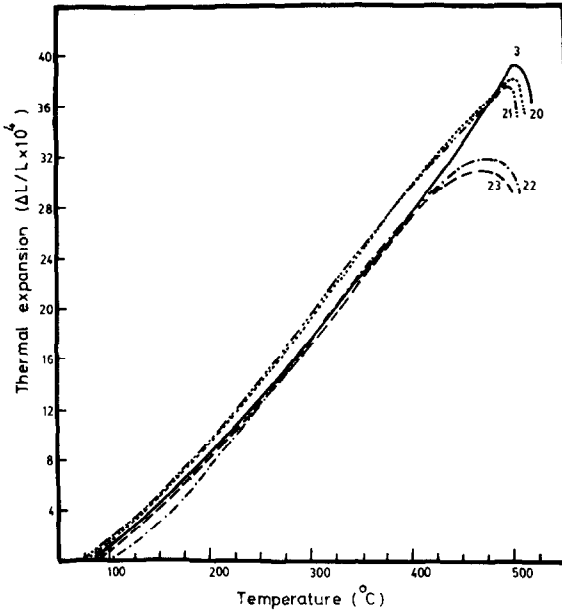
Fig. 6. Thermal expansion curves of lead silicate glasses containing MgO (3) 80% PbO, 20% SiO_2, 0% MgO; (20) 79% PbO, 20% SiO_2, 1% MgO; (21) 78% PbO, 20% SiO_2, 2% MgO; (22) 75% PbO, 20% SiO_2, 5% MgO; (23) 70% PbO, 20% SiO_2, 10% MgO.
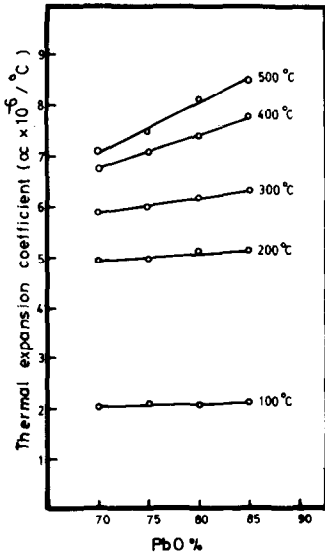

Fig. 7. Thermal expansion coefficients of $PbO-SiO_2$ glasses.

Fig. 8. Thermal expansion coefficients of lead silicate glasses containing B_2O_3.

Fig. 9. Thermal expansion coefficients of lead silicate glasses containing CaO.

Fig. 10. Thermal expansion coefficients of lead silicate glasses containing SrO.
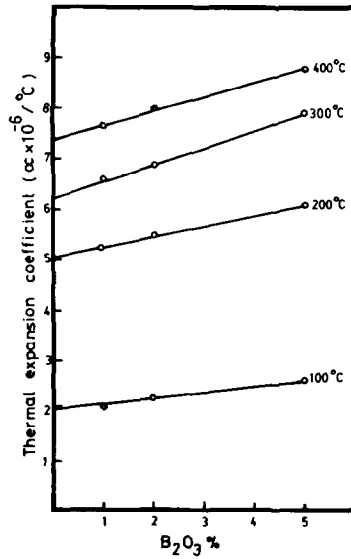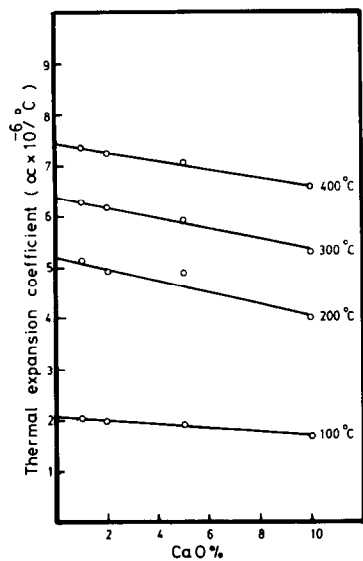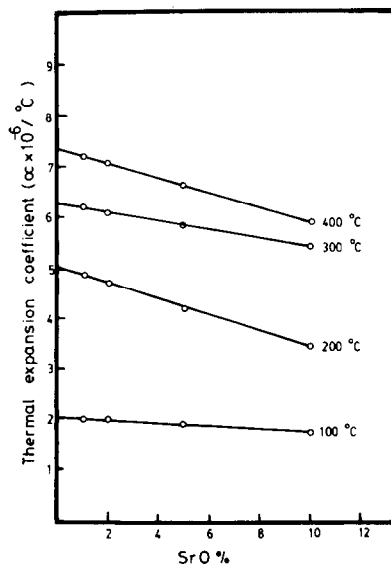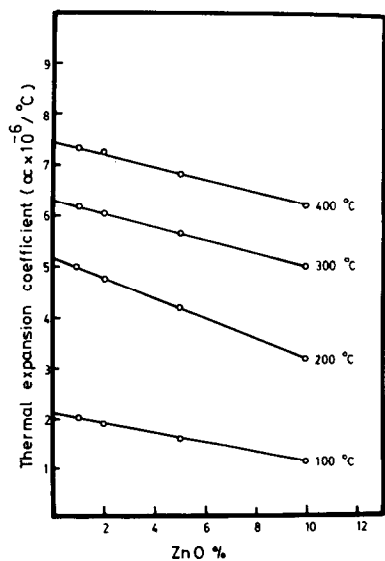

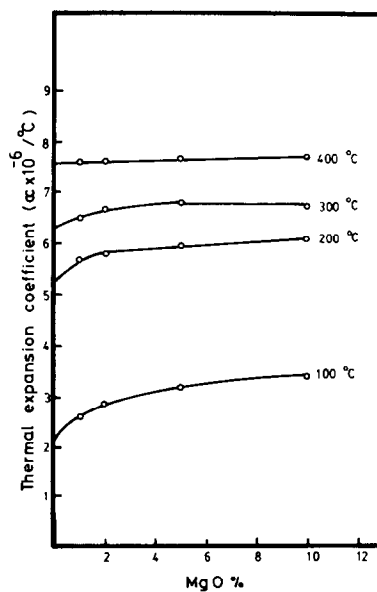Fig. 11. Thermal expansion coefficients of lead silicate glasses containing ZnO.

Fig. 12. Thermal expansion coefficients of lead silicate glasses containing MgO.

one of the divalent oxides, CaO, SrO or ZnO replacing PbO, it is seen that the thermal coefficient α decreases and the transformation temperature increases. The addition of MgO increases the thermal coefficient α and decreases the transformation temperature.

DISCUSSION

The expansion of a glass depends mainly on the internal network structure, the arrangement of the individual building units and their bonding to each other. Since the individual atoms in the structure are held by a balance of attractive and repulsive forces, the addition of thermal energy to the structure upsets the balance and an increase in length is noted.

Mechanism of thermal expansion

It was stated earlier [5] that expansion in crystals is due to two types of movement. In the first type, the whole structure expands by increase of scale, with expansion coefficients much the same in all directions, and there is no large change in bond angles. In the second type, besides the change in scale, an expansion of the lattice can result from change in bond angles with temperature, without change in bond length. Douglas [6] argued that because of the nature of glass, configurational changes corresponding to changes in the distribution of bond lengths, bond angles, etc., will necessarily occur with variation in temperature.

Later, Hummel [7] concluded that the change in bond angles seems to be a major factor in most instances of volume changes due to thermal expansion. This comes from the observation that all crystalline silica phases, with few exceptions, have higher coefficients of expansion than glassy silica. An alternative view is the assumption of Warren [8] that the expansion is only due to vibration of cations.

A model for simple pure glass was proposed by Smyth [9] and Kumar [10] in which, during expansion, the distances between equilibrium positions of the atoms of the glass increase in the same ratio. In the building lattice the ions vibrate about their respective equilibrium positions with amplitudes that go on increasing with rise in temperature. From lattice energy considerations the ionic vibrations are anharmonic and as a result, with increasing amplitude of vibration, the interionic distance increases. The ions are vibrating independently of each other.

The frequencies of vibrations in vitreous silica are grouped as follows:

(a) V_{si} or frequency of vibration of Si^{4+} ion; Si^{4+} being surrounded tetrahedrally by O^{2-} in a cubic field;

(b) V_L or frequency of longitudinal vibration of oxygen along Si–O–Si;

(c) V_T or frequency of transverse vibration of oxygen along the two axes perpendicular to Si–O–Si.

Smyth [9] and Kumar [10] considered that the thermal expansion of vitreous silica is primarily due to longitudinal vibration of oxygen along the Si–O–Si line. It is likely that the negative expansion in vitreous silica arises from transverse modes in the Si–O–Si network and that some of these modes are of low frequency to account for the very large magnitude of the negative coefficient at the lowest temperatures [11].

Weyl and Marboe [2] 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 short range order of glasses and increase the thermal vibrations. The very low thermal expansivity of vitreous silica at ordinary temperature reveals strong forces and highly symmetrical short range order.

It was also postulated that [11–15] the low expansivity of silica glass with no modifiers is expected from its open structure with certain vibrational modes of the oxygen ions along the Si–Si axis. With the introduction of any alkali or other network-modifying ions which occupy the interstices of the structure, these help to supply a restoring force for transverse oxygen displacements which increase as the structure shrinks and thereby tend to give a positive expansion.

Interpretation of the results

It is a generally accepted rule [16] that in most known cases involving compositional manipulation of glasses, the coefficient of thermal expansion increases when the softening point decreases. Previous studies [17] on the softening points of lead silicate glasses revealed that the softening point decreased as the lead oxide content increased. With the divalent metal oxides replacing lead oxide, the softening points increased in the order magnesium (greatest increase), calcium, strontium, zinc. The relative effects of these oxides were related to the field strengths and ionic sizes of the cations.

It was previously stated [18] that the thermal expansion could be governed by the bond strength and the bond character of the glass. The consideration of the experimental values show that the single bond strength is not the only major factor controlling thermal expansion. To explain the relatively high thermal expansion and the different effects of the various factors, the internal structures of such glasses are to be considered with the particular response on the vibrational modes.

Earlier studies [19–21] on lead glasses assume that in lead oxide–silica glasses in which the PbO content is low, the Pb^{2+} ions will be mostly enclosed within the interstices formed between the SiO_4 tetrahedra. In glasses containing larger amounts of PbO, some of the lead atoms apparently act as network-formers. Further X-ray diffraction investigations of lead

silicate glasses [22] and of crystalline PbO [23] established the existence of chain-like PbO units. The data for $PbO \cdot 2 \, SiO_2$ glass were interpreted suggesting that the structure consisted of a simple, nearly straight chain, those for $PbO \cdot SiO_2$ glass in terms of a twisted spiral chain, and those for $2 \, PbO \cdot SiO_2$ glass is in terms of an even sharper spiral chain. The apparent polymeric characteristics of PbO chains may explain the relatively wide glass-forming range in the system $PbO \cdot SiO_2$. Recent Raman studies confirm the previous assumptions [24]. The increase of the thermal expansion coefficient and the rapid decrease of the transformation temperature with the increase of PbO content in glass might be thought to be due to the less rigid or loosely compact nature of the structure [19–24].

A similar conclusion was arrived at by thermal expansion measurements on borophosphate glasses [25]. A recent view is advanced [26] to explain the differing effects that Na_2O and PbO additions have on the silica glass structure and their effects on the thermal expansion at low temperatures. Soda is considered destructive and lead oxide constructive of the glass network. If the Na^+ ions are destroying the bridging oxygen bonds, then the negative contribution to the thermal expansion coefficient will be much reduced as a greater proportion of such bonds are attacked. In contrast, the Pb^{2+} ions may damp but not completely destroy the transverse vibrational modes, producing a smaller change in per mole% of PbO.

To realize that the addition of boric oxide replacing silica in such high lead silicate glasses increases the thermal expansion coefficient and decreases the transformation temperature, we may suggest that the boron in such glasses mostly assumes the four coordination state with oxygen [20,21]. Thus tetrahedral boron groups possess a lower single bond strength (89 cal $mole^{-1}$) compared with that of silica in tetrahedral coordination (106 cal $mole^{-1}$). This is consistent with the recently published data [27] on thermal expansion coefficients of some high lead glasses which show that glasses containing boric oxide give higher values than the corresponding glasses containing silica.

The relative differing effect of the divalent oxides studied can be understood when it is recalled that replacing Pb^{2+} with a single bond strength (36 cal $mole^{-1}$) by one of the divalent Ca^{2+}, Zn^{2+}, Sr^{2+} with single bond strengths 32, 36 and 32 cal $mole^{-1}$, respectively, will be expected to decrease the thermal expansion coefficient while Mg^{2+} will presumably increase the thermal expansion coefficient.

The results of glasses containing magnesium can also be realized when it is considered that four-coordinated Mg^{2+} is assumed to be present in extremely basic glasses [28] and it is possible that high lead glasses favour this tendency.

The possible presence of heterogeneities described by Liedberg et al. [29] to be found in the internal structure of optically homogeneous high lead glasses, is assumed not to affect substantially the thermal expansion, as these heterogeneities are postulated to be present as regions of similar texture.

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