

Thermal expansion of lead silicate glasses

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The thermal expansion, when heated from 77 to 273 K, of two samples of lead silicate glass, containing 21 and 28.5 mol % PbO, has been measured. The temperature dependence of the thermal expansion coefficient, α , is in qualitative agreement with the expansion behaviour of sodium silicate glass. However, the addition of ~ 21 mol % PbO to silica is required to produce an increase in the magnitude of α comparable to the addition of only ~ 10 mol % Na₂O. The differences in the magnitudes of α for lead and soda glasses are considered in the light of previous proposals for their structures.

1. Introduction

A variety of observations have been made in recent years in an effort to identify the structure and provide a better understanding of the behaviour of binary silicate glasses. Measurement of electrical, magnetic, thermal and mechanical properties have been made but, of all the physical properties, the thermal expansion seems particularly sensitive to changes in composition. For instance, the coefficient of thermal expansion of silica at room temperature is increased ten-fold by the addition of 10 mol% soda [1].

Technical applications, such as delay line devices, have stimulated interest in the physical and structural properties of lead silicate glasses, the subject of a recent review by Rabinovich [2]. The relative ease with which glasses can be formed with high lead content has enabled expansion measurements to be made on samples containing as much as ~ 70 mol% PbO. There remains a distinct lack of data for compositions containing less than ~ 30 mol% PbO and the data which are available are mainly concerned with expansion at or above room temperature [3-5]. The paucity of low temperature expansion data became evident when results of low temperature ultrasonic experiments were being studied, for it had been considered that a comparison of the ultrasonic and thermal expansion data could be useful. The present experimental investigation was conducted to complement the ultrasonic data and provide some insight into the structure and behaviour of binary lead silicate glasses.

2. Experimental techniques

Two glasses were prepared with nominal compositions of 50 wt% and 60 wt% PbO (~ 21 mol% and 28.5 mol%, respectively). Melting was performed in a platinum crucible with a platinum stirrer. A melting temperature of 1550°C was used although this was raised to 1590°C for pouring. The finished glasses were annealed at 560°C for three hours. The annealed samples were examined with polarized light and found to be free of residual stress. Room-temperature densities (Fig. 1) compare favourably with three independent sets of density determinations in the compositional range 20 to 68 mol% PbO by Abou-el-Azm and Hussein [6], Demkeena [7] and Shaw and Uhlmann [8]. Disc-shaped specimens, about 8 mm diameter and 1 mm thick, were prepared and strain gauges (Micromeritics type SK.09-015 DJ), specially selected for thermal expansion measurements above a temperature of 77 K, were bonded to the flat faces with BR600 adhesive. An identical gauge was bonded to a disc of pure silica. The gauge on each lead glass sample was incorporated in turn in a direct current bridge network, with the gauge mounted on silica in the opposite side of the network. Hence the thermal expansion of the lead glass may be compared with that of silica. Employing data for thermal expansion of pure silica [9], the expansion of lead glass can be determined. Automatic temperature control enabled temperatures to be varied in the range 77 K to room temperature with a stability better than ± 0.1 K, each measurement of the expansion being made at

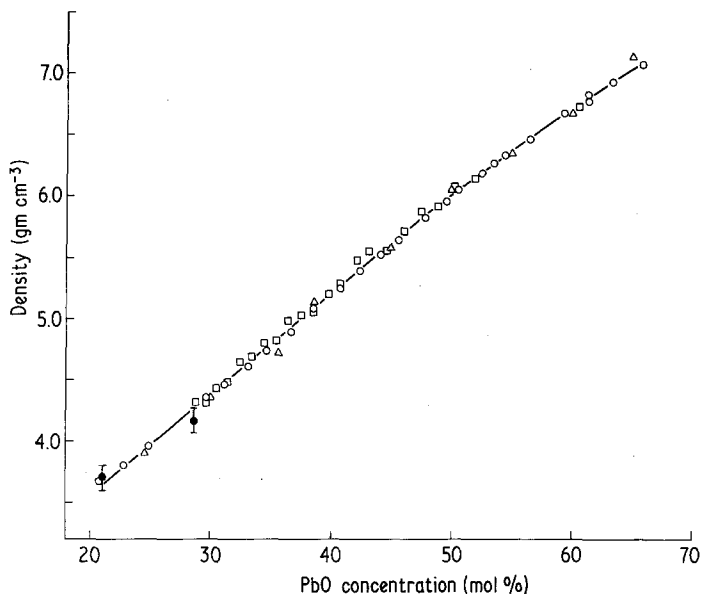


Figure 1 Density of lead silicate glasses at room temperature as a function of PbO-content. ● present data, □ data from [6], ○ data from [7], △ data from [8].

temperature intervals of ~ 3 K. Temperatures were measured with a gold + 0.03 at% iron/chromel thermocouple capable of resolving temperature changes of ± 0.05 K with an absolute accuracy of ± 0.5 K. Further details of these experimental techniques can be found in a previous publication [10].

Taking into account the strain resolution of the gauges and the bridge network ($\pm 0.04 \mu\text{m}$ strain) and accumulative errors from any mismatch of inherent strain gauge resistance during cooling, the thermal expansion coefficient, α , was measured directly to an accuracy of $\pm 0.1 \text{ K}^{-1}$ at room tem-

perature and $\pm 0.2 \text{ K}^{-1}$ at liquid nitrogen temperature. Values for the expansion coefficient were also determined from the gradient of a polynomial, fitted by a "least-squares fit" computer program to data for thermal strain as a function of temperature (Fig. 2). A comparison of the values of α obtained from the two methods is shown in Fig. 3 for 21 mol% PbO glass.

3. Results and Discussion

From room temperature to 77 K the thermal contraction of the lead glass containing 28.5 mol% PbO is greater than that containing 21 mol%

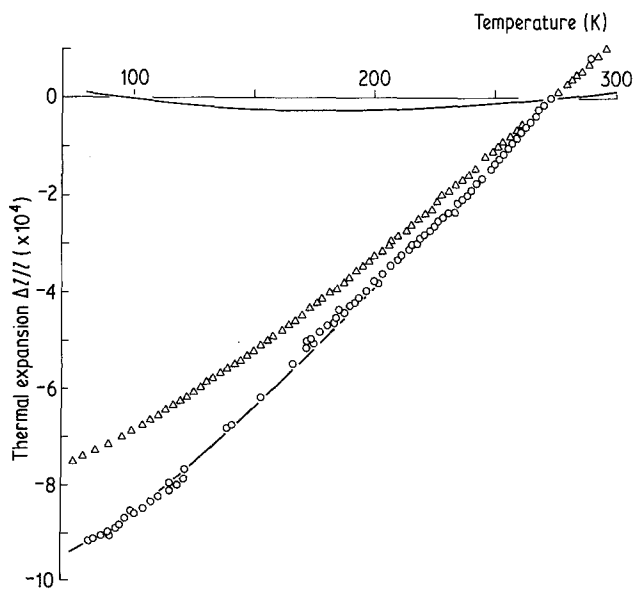


Figure 2 Thermal expansion of 21 mol% PbO (Δ) and 28.5 mol% PbO (\circ) lead silicate glasses as a function of temperature. The solid line indicates the thermal expansion of pure silica [9].

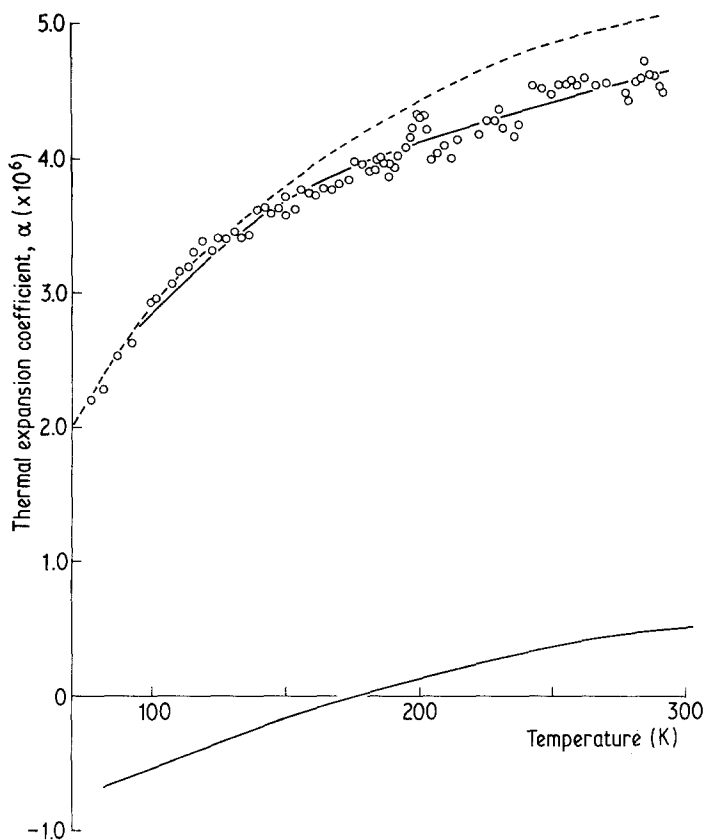


Figure 3 Thermal expansion coefficients of lead and sodium silicate glasses as a function of temperature. —○— Present data for 21 mol% PbO lead silicate glass obtained by direct measurements together with the coefficient derived from a curve fit to data in Fig. 2. — (solid line) expansion coefficient of pure silica, from [9]. - - - (broken line) expansion coefficient of 10 mol% soda glass, from [1].

(Fig. 2) and the anomalous expansion exhibited by silica for temperatures below about 180 K [11] is no longer apparent. Data for the expansion coefficient, α , (Fig. 3) from 21 mol% PbO confirm, within the temperature range covered by the present investigation, that the thermal expansion coefficient remains positive. The rapid decrease in α near 77 K, similar to the behaviour observed in soda glasses [1], suggests that the expansion coefficient changes sign at a lower temperature. Measurements down to 4.2 K are in progress to investigate this possibility.

The most obvious departure of lead silicate glass from the behaviour of silica is seen at temperatures well above 77 K, the room temperature thermal expansion coefficient in 21 mol% PbO glass, for example, being approximately ten times that for pure silica. This is a feature of the data for soda glass [1] with the room-temperature expansion coefficient increasing from about $0.5 \times 10^{-6} \text{ K}^{-1}$ for pure silica to about $5 \times 10^{-6} \text{ K}^{-1}$ for 10 mol% soda glass. It appears that for both lead and soda glasses, as the temperature is decreased, the thermal expansivity reverts to a behaviour more characteristic of pure silica and the effects

of the PbO and Na₂O on the vibrational spectra of the basic silica structure become less significant.

It is important to realise, however, that although these similarities in the temperature dependence of α in lead and soda glasses are apparent, a quantitative comparison shows that the addition of Na₂O has twice the effect on the magnitude of α , as does an equal molecular percentage of PbO. The expansion coefficients at any temperature in the range 77 K to 293 K are almost identical for 10 mol% Na₂O to 21 mol% PbO (Fig. 3) and the room-temperature coefficients for equal percentages of PbO or Na₂O are approximately in the ratio 2:1 for a wide range of composition (Fig. 4). This comparison now suggests that the roles played by Na₂O and PbO in modifying the structural dynamics are different.

The changes of the vibrational spectra due to the additions of PbO or Na₂O must be due, in part, to modification of the basic silica structure. It is pertinent to review the proposed structures of soda and lead silicate glasses to find reasons for their similar qualitative behaviours and simultaneously to explain the more pronounced increase in the value of α due to addition of soda.

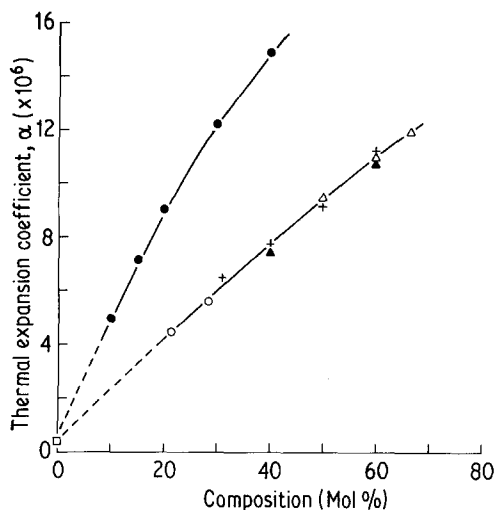


Figure 4 Thermal expansion coefficients of lead and soda glasses at room temperature as a function of composition. \circ Present data, \dagger [3], \blacktriangle [4], \triangle [5], \bullet soda glass data (after [1]), \square pure silica, [9].

Early discussions of the structure for soda glass were based on a network modifying role for the sodium ions. X-ray diffraction studies [12] suggested that Na^+ ions occupy spaces or "voids" in the vicinity of the original silica network, ionically bonded to oxygen ions which had hitherto been singly bonded in the silica network. Recently, it has been proposed [13] that soda glass is a "substitutional" compound in which soda replaces SiO_2 molecules, otherwise the density would be much greater than that actually observed in, say, 30 mol% soda glass. According to Urnes [14], a local structure develops in which one oxygen ion, originally forming a bridging bond in the silica chain, is replaced by two non-bridging oxygens and two sodium ions. The addition of soda has a disruptive effect on the network, with each Na^+ ion strongly bonded to one oxygen ion, consequently weakening the glass structure at this point. Kruger [13], in the light of specific heat and thermal conductivity data, and Gross *et al.* [15] who studied the Raman spectrum, both refer to this structural weakening.

Glasses with high lead content are relatively easy to form even though Pb^{2+} ions lack the small size and high charge which used to be considered essential in the original concept of a good network former. Later it was appreciated that the mutual polarization of the O^{2-} and Pb^{2+} ions play an important part in the bonding and recent evidence from X-ray diffraction [16] and Raman spec-

troscopy [17] confirm the readiness with which Pb^{2+} ions participate in a glass forming network, at least in glasses with high lead content. Estimates of density for samples used in the present work suggest that lead glasses, like soda glass, are "substitutional" compounds. The density of 21 mol% PbO glass is expected to be about 5.7 gm cm^{-3} if the Pb^{2+} enters vacancies but about 4.0 gm cm^{-3} if PbO is substituted into the original silica structure. The measured density of $3.7 \pm 0.1 \text{ gm cm}^{-3}$ is closer to the latter of the two estimates and is consistent with the concept of Pb^{2+} as a network former. Furthermore, Mydlar *et al.* [16] report strong evidence from X-ray diffraction studies that at 50 mol% PbO and above, the lead ions take regular positions in the silica chains and provide some evidence of network forming at 33 mol% PbO . A model emerges in which the transition from pure silica to crystalline orthorhombic PbO is accomplished by a gradual progression through linear, coarse and fine helical chain structures, with the Pb^{2+} ion in a constructive role.

In view of the differing effects that Na_2O and PbO additions have on the glass structure, being destructive and constructive respectively, it is difficult to explain both the similarity of the expansion coefficients as depicted in Fig. 3 and their ratios at room temperature shown in Fig. 4. It has been proposed that in soda glass [1] the sodium either strongly inhibits the transverse vibrational modes of the oxygen atoms which bridge adjacent silica tetrahedra, leading to a negative expansion coefficient, or perhaps introduces new modes of vibration which make a positive, direct contribution to the thermal expansion. X-ray evidence [16, 18] suggests that the most likely inter-ionic distances for sodium ions and lead ions are almost equal and hence a positive contribution arising from direct interactions between the cations is unlikely to account for the differences between the expansion coefficients of lead and soda glasses. It is more likely that modifications to the transverse vibrational modes are critical. 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 α per mol% of PbO lead silica glass than could be expected for soda glass.

It is notable from the data currently available (Fig. 4) that the expansion coefficient, which is susceptible to changes in structure, varies smoothly in the range 21 mol% to 70 mol% PbO lead silicate glass, which is in keeping with the gradual structural changes proposed by Mydlar *et al.* [16] from results of X-ray studies.

In conclusion, it appears that the thermal expansion data presented here are not at variance with the corresponding behaviour of soda glasses, the previous theories for the origin of the negative expansion coefficients in silica and soda glasses or with the proposed structures for lead and soda binary silicate glasses. More positive evidence for the positions of Pb^{2+} and Na^+ ions in the silicate glass structures would be invaluable. Further measurements of thermal expansion and ultrasonic properties are already in progress on samples with a much wider range of composition.

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