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Unusual thermal expansion behaviour of PbO-rich PbO–B_2O_3 glasses

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An unusual discontinuity in the thermal expansion behaviour of a 36 PbO–64 B_2O_3 wt % phase-separated glass was examined. Expansion tests combined with other experimental techniques established a correlation with a structural rearrangement in the cracked particles of the dispersed phase.

1. Introduction

Among the phase-separated glassy systems, PbO–B_2O_3 is one of the best characterized. The miscibility gap lies between about 1 and 44 wt % PbO [1]. The microstructures observed at all compositions within the miscibility gap consist essentially of spherical particles of one phase in a continuous matrix of the other phase, as shown in Fig. 1. The literature is rich with information on this system: for instance, there are pages dealing with density [2], elastic [3], mechanical [4, 5], thermal and chemical [6] properties.

Thermal expansion curves are reported by Shelby [6]. For compositions belonging to the PbO-rich side of the miscibility gap (between about 30 and 44 wt % PbO), the curves are similar to that shown in Fig. 2. By inspecting this figure, it is easy to point out the glass transition temperature, T_{gM}, of the continuous phase which, in this case, is a glass with 44 wt % PbO. Near the glass transition of the dispersed phase, almost pure glassy B_2O_3, a small inflection (point A) and a sharp discontinuity (BC line) are evident. At first consideration one might expect a thermal expansion pattern which shows only two inflections corresponding to the T_g of the two glassy phases.

To our knowledge, none of the authors who have studied this system have explained this unusual thermal expansion behaviour. The aim of this paper is to give new experimental data in order to gain better insight into this effect.

2. Experimental details and results

Glass samples, 36 PbO–64 B_2O_3 wt %, have been obtained by melting pure chemical reagents (H_3BO_3, Pb_3O_4) in a platinum crucible at 950° C, casting in stainless steel moulds, annealing for 30 min at about 450° C and cooling at 5° C min^{-1}.

A typical thermal expansion pattern of this glass, obtained with a Netzsch fused silica dilatometer model 402E, is shown in Fig. 3. This curve agrees very well with that of Shelby [6], shown in Fig. 2. The thermal expansion coefficient between 20 and 200° C is $75 \times 10^{-7}\,{}^\circ C^{-1}$ in good agreement with the literature [6]. The glass transition temperature of the matrix, T_{gM}, is about 420° C, the first inflection (point A) about 230° C, and the step (BC line) between 270 and 300° C. First, it was decided to verify if this behaviour was reproducible. For this purpose two dilation tests were made in sequence on the same sample (Fig. 4) also recording the thermal contraction on cooling. The maximum temperature (370° C) has been chosen in the middle between the end of the discontinuity (300° C) and T_{gM}. Curve a in Fig. 4 shows that on cooling the sample did not return to the initial length but retained a 0.034% residual elongation. Curve b, obtained by repeating the test on the same sample, shows a very different behaviour: the discontinuity has practically disappeared and, on cooling, the glass recovers the initial length, without any residual elongation. The thermal expansion coefficient between 25 and 200° C is essentially the same in both measurements.

Additional experiments have revealed that after a glass specimen is reheated to a temperature between 300 and 400° C (point C and point T_{gM} on Fig. 3), it invariably displays a thermal expansion pattern similar to that shown in Fig. 4b, without the discontinuity and without the residual expansion. On the other hand, if the specimen is reheated above 400° C, i.e. above T_{gM}, the thermal expansion behaviour reverts to that shown in Figs 2 and 3.

To clarify the cause of the different thermal expansion patterns, a differential scanning calorimeter

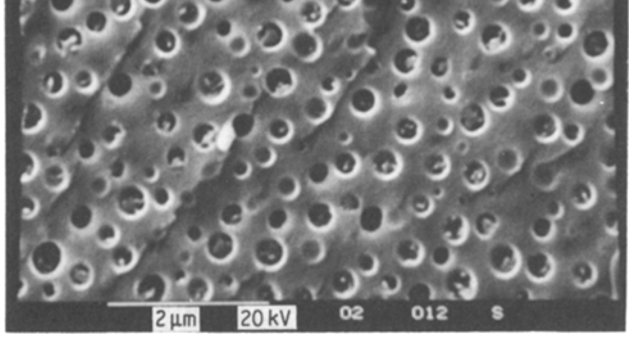

Figure 1 Fracture surface of a 36 PbO–64 B_2O_3 wt % glass sample, cast from 950° C in stainless steel moulds, showing B_2O_3-rich particles in a PbO-rich matrix.

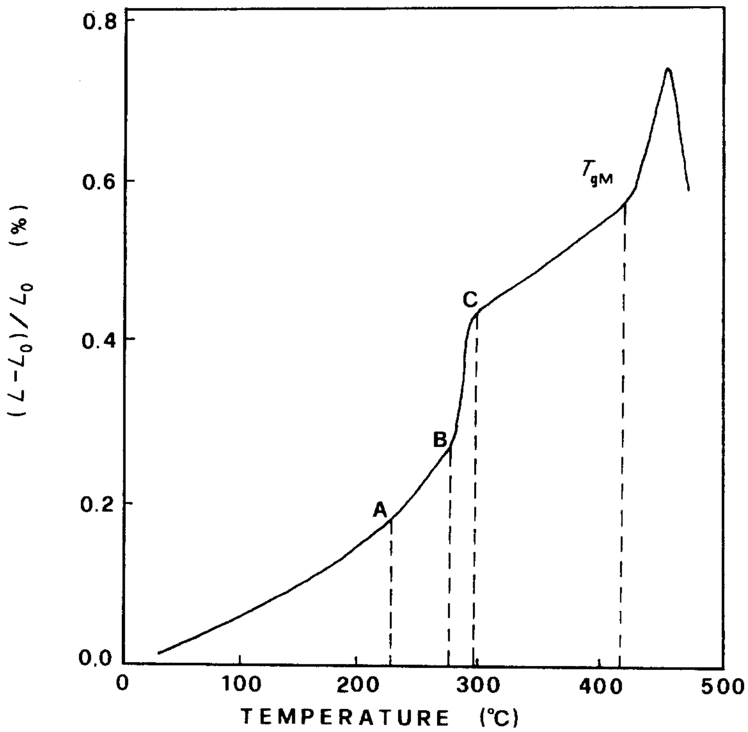

Figure 2 Thermal expansion curve, as reported by Shelby [6], for a 30 PbO–70 B_2O_3 wt % glass.

(DSC) and a scanning electron microscope (SEM) were used along with elastic modulus and fracture toughness measurements on as-cooled glass (sample I) and on glass reheated to 360° C (sample II). SEM investigations (Cambridge Stereoscan), made on fresh fractured surfaces, do not exhibit any substantial difference between the two samples. Fig. 1 is a scanning electron microscope of sample I. DSC (Netzsch mod. 444) measurements have exhibited the following features.

For sample I:

1. An endothermic effect between 260 and 270° C, due to the glass transition of the dispersed phase.

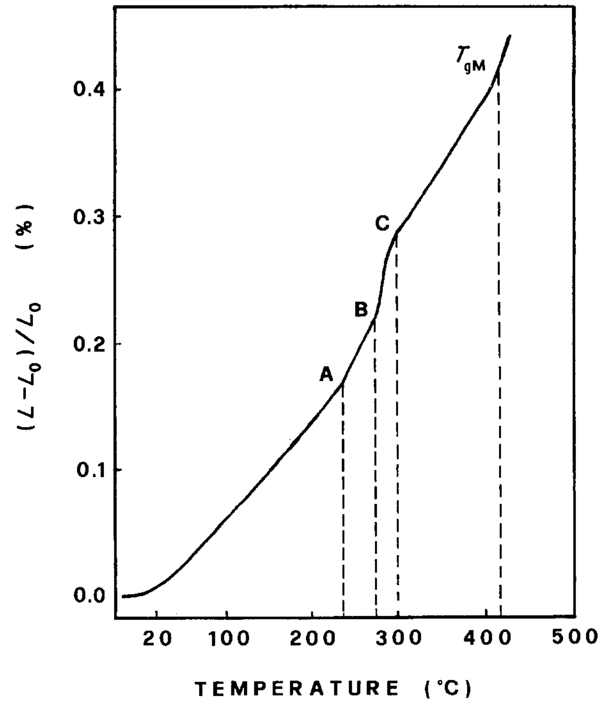

Figure 3 Thermal expansion curve of a 36 PbO–64 B_2O_3 wt % glass sample.

2. Small exothermic peak at 290° C.
3. Endothermic effect at about 440 to 450° C, due to the glass transition of the continuous phase.

For sample II:

1. An endothermic effect at about 270 to 280° C.
2. An endothermic effect at about 430 to 460° C.
3. Absence of the exothermic peak shown by sample I.

The dynamic elastic modulus tests, made by measuring the resonance frequency on bending, have not shown any difference between the two samples. The "critical stress intensity factor" measurements, made by identation according to the Evans and Charles formulation [7], gave these values:

sample I $K_{\mathrm{Ic}} = 0.80 \pm 0.005$ MPa $\mathrm{m}^{1/2}$

sample II $K_{\mathrm{Ic}} = 0.85 \pm 0.005$ MPa $\mathrm{m}^{1/2}$

3. Discussion

On cooling from the liquid state, a stress field arises in the glass due to the thermal expansion mismatch. Since the dispersed phase has a thermal expansion coefficient higher than that of the matrix, residual stresses, as shown also by other authors [4], are tensile in the spherical particles, radial tensile and tangential compressive in the matrix. These stresses arise on cooling as soon as the continuous phase is in the elastic range, i.e. below T_{gM}. At temperatures between T_{gM} and T_g of the dispersed phase, the spherical particles behave like a fluid, sustaining only hydrostatic stresses. Below this range of temperatures both phases are purely elastic. Scherer [8] recently presented a careful viscoelastic analysis of the thermal stresses that grow up in this kind of phase-separated glasses. Shinkai *et al.* [5], studying a glass of the same composition and with spherical particles having dimensions comparable to those in the present glass, have shown that the tensile stress within the dispersed phase

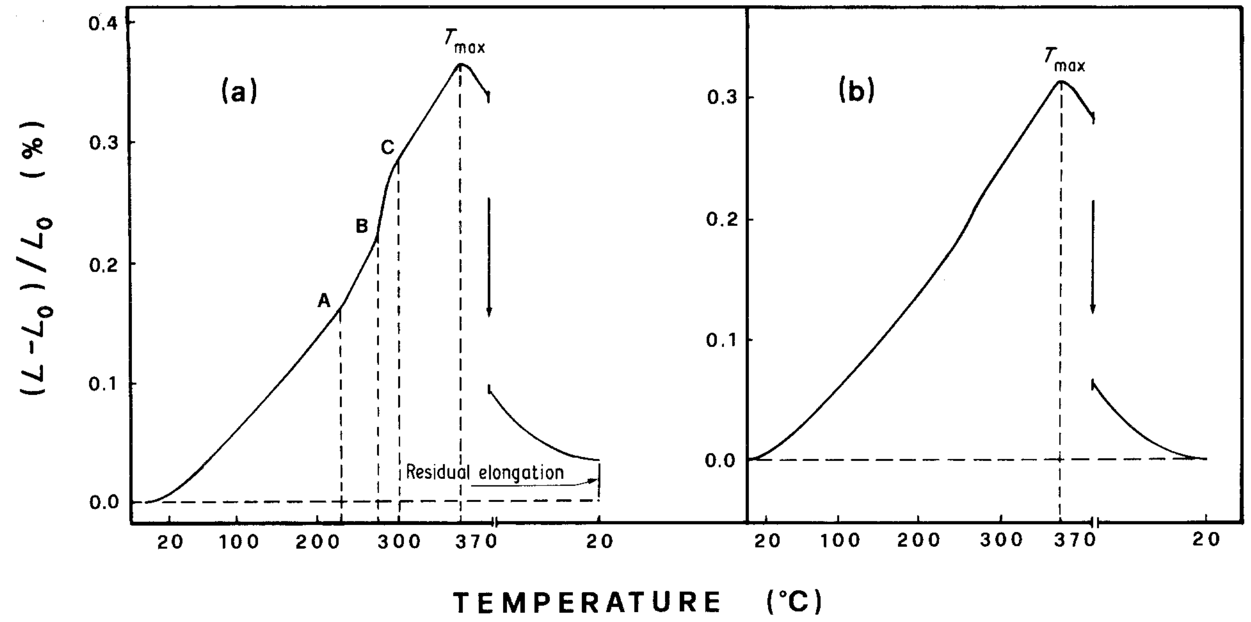

Figure 4 Thermal expansion curves of: (a) as-cooled sample (sample I); (b) the same sample after test a (sample II).

may be so high as to produce in some of the large droplets microcracks which extend directly through the particles. Crack formation necessarily partly relaxes the stresses grown up in the elastic range. On the other hand, the tensile stresses arisen in the fluid range are frozen because their relaxation may occur only by a structural rearrangement at a temperature near the T_g of the dispersed phase. On heating, at that temperature, the cracked spheres reduce their tensional stresses, the matrix is no longer constrained by this tension, and hence it is free to expand towards its unconstrained volume, causing both the expansion discontinuity, BC, and the residual elongation recorded in the thermal expansion apparatus (see Fig. 4, curve a).

In the latter test, curve b, neither the discontinuity (BC line) nor the residual elongation are observed because the hydrostatic tensile stresses have already been relaxed in the former test. Heating the sample to a temperature higher than T_{gM}, the structural continuity is restored in all the particles of the dispersed phase and, on cooling, the hydrostatic tensile stresses arise again: the sample is then in the starting condition and indeed its dilation curve is the same as sample I.

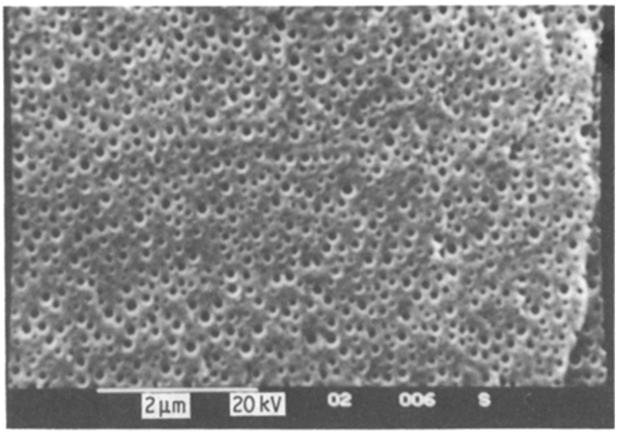

Figure 5 Scanning electron micrograph of a fresh fractured surface relative to the sample quenched in liquid nitrogen.

The suggested model is also consistent with other performed measurements. The structural rearrangement which produces the relaxation of the hydrostatic stresses in the cracked particles would be accompanied by heat generation. Indeed, DSC tests made on sample I show an exothermic effect at 290° C, a temperature very near to the end of the discontinuity (point C) present in the dilatation pattern. On the DSC curve of sample II this exothermic effect is missing, neither is there the discontinuity in the dilatation pattern. On the grounds of the proposed model, the difference between sample I and sample II is: in sample I the cracked particles retain the structural stresses which arose on cooling in the fluid range that are, on the contrary, relaxed in sample II.

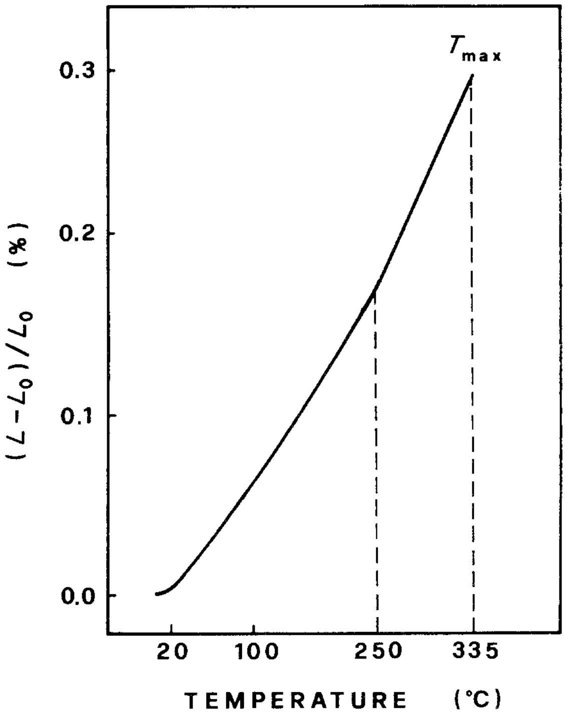

Figure 6 Thermal expansion curve relative to the sample quenched in liquid nitrogen.

The existence of a small but not negligible difference in the K_{Ic} value between samples I and II is consistent with the proposed model. In fact crack propagation is affected by residual stress fields. The fact that the values of the elastic modulus and the thermal expansion do not change from one sample to the other can be explained by considering that the difference between the two samples is not large enough to justify possible changes of these physical properties.

The proposed model implies that if it is possible to avoid the formation of cracks in the dispersed phase, then the thermal expansion curve will not show the discontinuity (BC line). Shinkai *et al.* [5] have shown that very fast cooling from the liquid phase largely reduces the size of the dispersed particles, and spheres without microcracks can be obtained. Thus, to confirm the model, glass samples have been prepared by quenching from the liquid state at 950° C between two copper plates cooled at liquid nitrogen temperature. The SEM investigations made on freshly fractured surfaces (Fig. 5), have shown that the average particles dimensions are much smaller than those of sample I.

The thermal expansion curve of the quenched sample is shown in Fig. 6. The absence of the typical step is clearly evident. The inflection at 250° C is due to the glass transition of the dispersed phase. As reported in the current literature [9], the glass transition temperature of pure glassy B_2O_3 is about 270° C; it is possible to ascribe this decreasing T_g to the hydrostatic tension of the B_2O_3 particles on cooling.

4. Conclusions

The discontinuity in the thermal expansion pattern of a glass 36PbO–64 B_2O_3 wt % is connected to a structural rearrangement in cracked particles at temperatures near T_g of the dispersed phase. This consideration is mainly supported by these experimental findings:

1. the step disappears until the sample is not heated to a temperature higher than T_{gM}; in such a case the structural continuity is restored in all the dispersed phase particles, renewing the initial configuration;
2. the structural rearrangement is accompanied by heat generation as indicated by DSC analysis;
3. the sample cooled in liquid nitrogen which in accordance with Shinkai *et al.*'s experimental observations [5], has very small particles without microcracks, shows a thermal expansion pattern with no discontinuity.

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