*Residual Stresses in Glass-Crystal Composites**

The effect of hydrostatic pressure on the transition temperature of various crystalline and noncrystalline materials has been studied extensively. The effect of internal stresses on the transition temperature, however, has received some attention for crystalline materials [1] and little attention for glasses. Assuming that internal stresses have the same effect on transition temperatures as hydrostatic pressures, a knowledge of such an effect on hydrostatic pressure can be used to calculate the internal stresses from the observed transition temperatures. This report investigates the experimental results for two glass-crystal composites. Lead titanate formed the dispersed phase, whereas Glass I and Glass II of compositions given in table I formed the matrices [2]. Thermal expansion coefficients of Glass I and Glass II are, respectively, 13.80 and 6.45 × 10^{-6} ° C^{-1}.

TABLE I Composition of glasses in wt %

	B_2O_3	BaO	Al_2O_3
Glass I	40	50	10
Glass II	80	10	10

Since lead titanate has negative expansion [3], the glasses in Glass I-lead titanate and Glass II-lead titanate will be in tension† on cooling from the hot-pressing temperature. Transition temperature of the glasses was determined from thermal expansion measurements.

Since the glass transition has been established to be second order [4], the thermodynamic relation

$$\frac{dt}{dp} = \frac{TV\Delta\beta}{\Delta C_p}$$

was shown to be applicable to glasses below a few kilobars, where T = transition temperature of glass; P = stress applied to glass; V = specific volume of glass; $\Delta\beta$ = difference in volumetric expansion coefficients of liquid and glass; ΔC_p = difference in specific heat of liquid and glass.

In an attempt to minimise the chemical reactions between glass and crystal, glass-crystal composites were heated at the rate of 50° C min^{-1}, hot-pressed for 2 min at 2000 psi‡ and air-cooled to room temperature in 5 min. Scanning electron microscopy of lead titanate particles before and after composite fabrication showed no difference, indicating the absence of any significant chemical reactions.

The measured values of these parameters for Glass I and Glass II are given in table I. The values of dT/dP, calculated using the observed values, are 31.0 and 29.5 per kilobar, respectively, for Glasses I and II. Since tension can be regarded as negative hydrostatic pressure, the transition temperatures of the glasses are, accordingly, lowered by the addition of lead titanate.

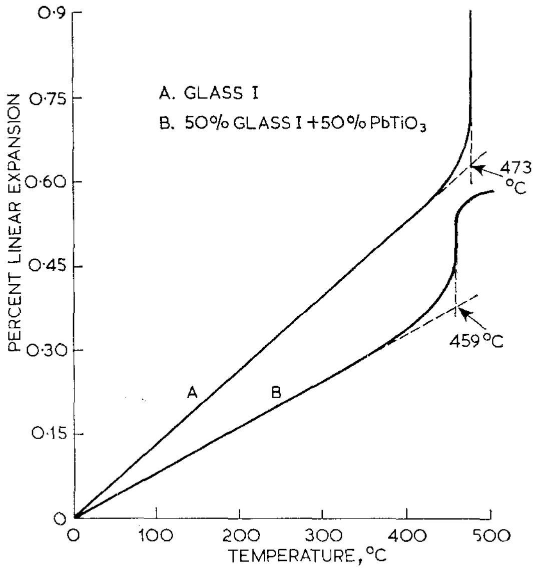

Figure 1 Transition temperature of Glass I as affected by internal stresses in Glass I-$PbTiO_3$ composites.

This is, in fact, observed as shown in figs. 1 and 2 for Glass I-lead titanate and Glass II-lead titanate composites. The temperature lowering was as much as 14° C for Glass I-lead titanate, and 10° C for Glass II-lead titanate. These values dropped to as low as 5° C and 3° C as the

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†Only the circumferential and axial stresses around each particle are tensile, while radial stresses are compressive. It is assumed that the contribution of the former dominates the latter.

‡1 psi = 6894.76 N m^{-2}.

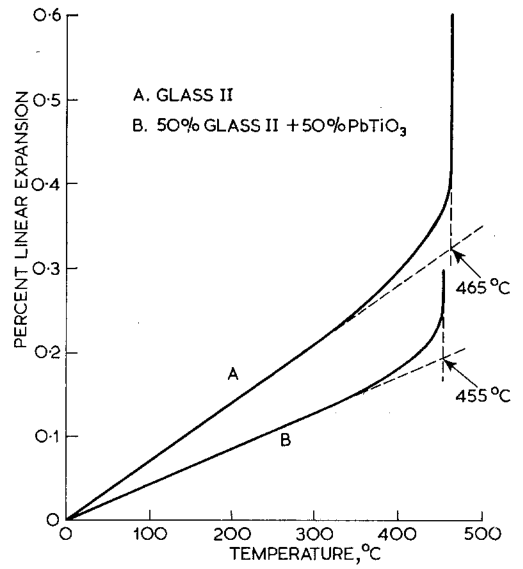

Figure 2 Transition temperature of Glass II as affected by internal stresses in Glass II-PbTiO$_3$ composites.

glasses were annealed. The stresses calculated from these shifts in transition temperature are 6300 psi for Glass I composites and 4600 psi for Glass II composites.

TABLE II Some Second order properties of glass I and glass II

Property	Glass I	Glass II
Transition temperature, ° C	473	465
Specific volume, cc gm^{-1}	0.42	0.25
Difference in volumetric expansion coefficient, ° C^{-1}	1.2×10^{-4}	1.8×10^{-4}
Difference in specific heat, cal gm^{-1} ° C^{-1}	0.03	0.028
dT/dp, ° C kbar^{-1}	31.0	29.5

It may appear at the outset that the stresses calculated from the changes in the transition temperature of glasses are considerably lower than expected. These are, in fact, very high and can be explained as follows: stresses in glass-crystal composites are developed due to the difference in expansion of the components as the composites are cooled from the hot-pressing temperature to room temperature. The magnitude of this stress (as can be calculated from the equations given in the literature [5, 6] is proportional to: (i) the cooling range, and (ii) the difference in expansion between the two components. To measure the transition temperature of glasses in glass-crystal composites, the composites are heated past the transition point to the softening point, where, again, no stresses exist. The stresses are maximum at room temperature; and, as the composites are heated, the stresses are lowered. In other words, only the stresses corresponding to the temperature difference between the transition point and the so-called upper no-strain temperature of glass can influence the transition temperature. The changes in the transition temperature of glasses are not reproducible from one run to the next on the same sample. This fact can be attributed to viscosity-time-temperature relations, since it is known that the residual stresses in glasses held at the transition temperature can be relieved with time.

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Temperature-Dependence of Characteristic Properties of α-Fe$_2$O$_3$ Powders

It has been shown in [1] that the "activity" of ferric oxide prepared by decomposition of various iron salts depends on the initial salts employed. Properties of ferric oxide also depend [2, 3] on its heat-treatment.

The aim of this note is to present the analysis (specific surface area, particle size and shape, particle size distribution and catalytic activity measurements) of α-Fe$_2$O$_3$ powders prepared by thermal decomposition of four hydrated iron salts (as in [1]) and calcined to different temperatures – 700, 900 and 1100° C.

The initial salts (hydrated ferrous sulphate,