

Section III. Rheology – transport properties

STRUCTURAL RELAXATION IN GEL-DERIVED GLASSES *

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Glasses with the same composition and hydroxyl contents were prepared by conventional melting and by hydrolysis of alkoxides. The differential scanning calorimeter (DSC) was used to compare the kinetics of structural relaxation of the glasses. Detailed examination of the data shows that there is no difference between them after the gel has been sintered near the glass transition temperature. Changing the oxide content of the melted glass causes significant changes in the DSC plots, so it is very important to confirm (as was done in this study) that the gel and melted glasses are identical in composition.

1. Introduction

It has been reported that gel-derived glasses differ from conventionally melted glasses in properties such as devitrification products [1], viscosity [2,3] and liquidus [4]. This is surprising, unless these glasses differ in composition, because structural rearrangements can occur in a matter of seconds at temperatures above the glass transition temperature, T_g . Therefore, significant structural differences between melted oxides and gel-derived glasses are not expected after the gel has been heated above T_g . The purpose of this study was to examine gels that had been sintered near T_g to see whether they differed from a melted oxide of the same composition. Great care was taken to insure that the oxide content and hydroxyl concentration were the same in both glasses. As in a previous study [5], we used a differential scanning calorimeter (DSC) to examine the kinetics of the relaxation of the enthalpy. The present data are more accurate than in the previous study, and the glasses are much closer in composition, but the conclusion is the same: no significant differences exist after the gel has been sintered near T_g .

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Table 1
Analyzed composition (wt%)

Sample	Na ₂ O	B ₂ O ₃	Al ₂ O ₃	SiO ₂	[OH] (ppm)
Sintered gel	7.71, 6.5	10.0, 10.7	1.0, 0.92	Bal.	2200
Melted gel	7.01	8.9	1.08	83	620
Desiccated gel	–	–	–	–	440
Melted oxide (A)	7.09	10.0	1.01	81.9	770
Melted oxide (B)	12	15	1	82	490

2. Materials

Table 1 shows the analyzed compositions of melted and gel-derived glasses. The sintered gel was analyzed independently (ICP) at both Corning and Sandia. The melted glasses were prepared from Supersil sand, B₂O₃, Al₂O₃, Na₂CO₃ and NaCl; the batch was ball milled, then melted and stirred for 6 h at 1600°C in a Pt crucible. The gel was prepared from silicon tetraethoxide, boron trimethoxide, aluminum sec-butoxide, and sodium acetate. The method of preparation was essentially as described in ref. 6. The target composition of the gel was that of melted oxide B in table 1; after the gel was chemically analyzed, oxide A was prepared to provide a better match. The relaxation kinetics of the two melted oxides were quite different.

Gel samples were sintered by heating to 650°C at 1°C/min in air. To reduce the OH content of the resulting glass, other samples of gel (called “desiccated”) were heated at 1°C/min to 400°C in air and held for 10 h, then heated to 500°C and held under a vacuum of 10⁻⁷ Torr for 24 h. The gels were then heated at 1°C/min in He to 650°C by which time they were completely sintered. One sample of gel was melted at 1325°C for 30 min (“melted gel”). The hydroxyl contents were found from the IR absorption at 2.7 μm, assuming an extinction coefficient of 56 l/mol cm [7].

3. Procedure

The heat capacity ($C_p = dH/dT$) measurements were performed in a Perkin-Elmer DSC2 differential scanning calorimeter controlled by a HP1000 computer; the peak error in C_p was < 2% and the RMS error was < 0.5% over the range (750–980 K) of the measurements. The samples were heated to 980 K in the DSC and held for 5 min, cooled at 0.62, 2.5 or 10°C/min, and reheated at 20°C/min. By integrating the area under the reheating curve, the fictive temperature T_f can be determined [8]. A plot of \ln (cooling rate) versus $1/T_f$ has a slope equal to $-\Delta H/R$, where ΔH is the activation enthalpy for the relaxation time and R is the ideal gas constant. Generally, ΔH is equal to the activation enthalpy for viscous flow. Fig. 1 shows the results for the

desiccated gel and the melted oxide (A, in table 1). The fictive temperature is defined by

$$H(T) - H(T_0) = \int_{T_0}^{T_f} C_{p_l} dT + \int_{T_f}^T C_{p_g} dT, \quad (1)$$

where T_0 is the starting temperature, and C_{p_l} and C_{p_g} are the heat capacities of the liquid and glass, respectively. According to the theory of Narayanaswamy [9], the fictive temperature is given by

$$T_f = T - \int_0^\theta M(\theta - \theta') \frac{dT}{d\theta'}, \quad (2)$$

where M is the relaxation function and θ is the reduced time defined by

$$\theta = \int_0^t \frac{dt'}{\tau[T(t), T_f(t)]}, \quad (3)$$

where τ is the relaxation time. The relaxation function is often [10] represented as

$$M(\theta) = e^{-\theta^b} \quad (4)$$

and the relaxation time is given by

$$\tau = \tau_0 \exp\left(\frac{x\Delta H}{RT} + \frac{(1-x)\Delta H}{RT_f}\right). \quad (5)$$

Thus, there are 4 parameters (τ_0 , ΔH , x , and b). ΔH is found from fig. 1, τ_0 is

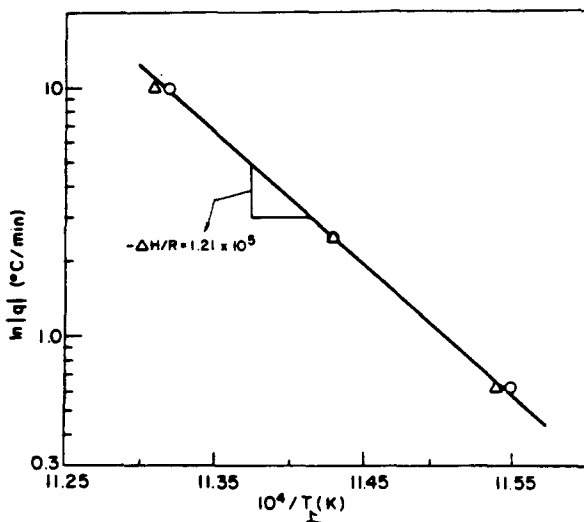


Fig. 1. Plot of $\ln(\text{cooling rate})$ vs. $1/T_f$; fictive temperature found by integration of DSC curve. Δ = desiccated gel, \circ = method oxide A.

chosen such that the correct T_f is obtained at the end of cooling, and x and b are fitted using the Nelder–Mead fitting algorithm [11].

As a check on the activation energy found from fig. 1, samples of the desiccated gel were sintered in a dilatometer. It has been shown [12] that the viscosity controlling sintering rises to a plateau value if the isothermal hold is long enough. Desiccated gel samples were sintered in a dilatometer at 585°C for 7000 min, 600°C for 4000 min, and 625°C for 120 min. The viscosity was obtained by fitting the densification data to a theoretical curve [13]. The times used were sufficient for the viscosity to plateau at each temperature, but the data at 585°C were erratic. Therefore, the activation energy was obtained from the temperature dependence of the plateau values at 600 and 625°C.

4. Results

The activation energy found from the sintering data was 183 kcal/mol., as compared to 240 kcal/mol. obtained from the DSC data (fig. 1). These are remarkably high values for an oxide glass (typically 120–170 kcal/mol.). Direct measurements of the viscosity of the melted glass will be performed to examine this unusual behavior.

The fits to the DSC curves were excellent; the best-fit parameters are given in table 2. In figs. 2, 3 and 4, the curves are drawn using the parameters for the desiccated gel. The curves have been shifted for clarity. Evidently, there is no significant difference between the melted oxides and the gels. When the melted oxide is compared to the sintered gel with a high OH content, the latter is found to have a lower T_g , but the shapes of the curves are the same. In contrast, if the oxide content of the melted glass is changed, the shapes of the curves change significantly. Fig. 5 compares two melted oxides (A and B in table 1) with different compositions that exhibit distinctly different relaxation behavior. This clearly demonstrates the importance of establishing the composition of both glasses when comparisons of this type are attempted.

The fitting parameters for the melted oxide (A) composition are unusual. The low value of b indicates a much broader distribution of relaxation times

Table 2
Fitting parameters

Sample	τ_0 (s)	x	$\Delta H/R$	b
Sintered gel	2.9×10^{-51}	0.77	106×10^3	0.45
Melted gel	1.2×10^{-65}	0.59	138×10^3	0.42
Desiccated gel	2.4×10^{-57}	0.61	121×10^3	0.43
			$(-91 \times 10^3)^a$	
Melted oxide (A)	1.0×10^{-58}	0.75	123×10^3	0.46
Melted oxide (B)	7.9×10^{-30}	0.71	64×10^3	0.80

^{a)} For viscosity from sintering data.

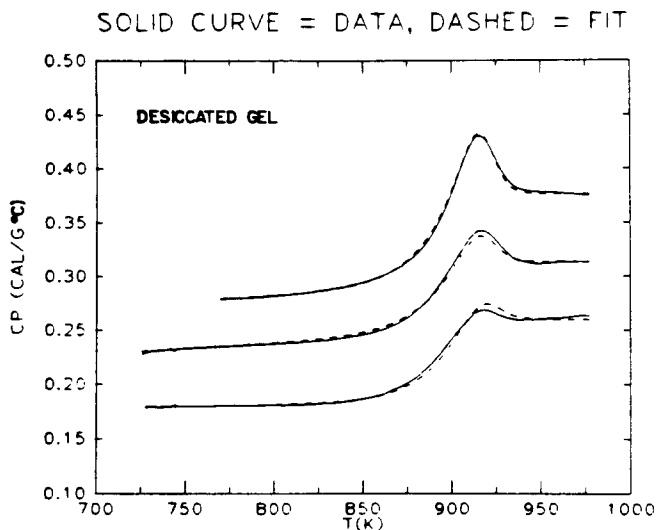


Fig. 2. Reheating curves for desiccated gel following cooling at 0.62 (top curve), 2.5, and 10 (bottom curve) $^{\circ}\text{C}/\text{min}$; curves shifted downward by 0.05 cal/g $^{\circ}\text{C}$ for clarity. Dashed curves calculated using best fit parameters from table 2.

than is typically found in silicate glasses. The activation energy is far higher than that governing the viscosity of similar glasses; for example, oxide B (see table 2) has the more typical value of 127 kcal/mol. Oxide A is clearly an interesting candidate for further studies in structural relaxation.

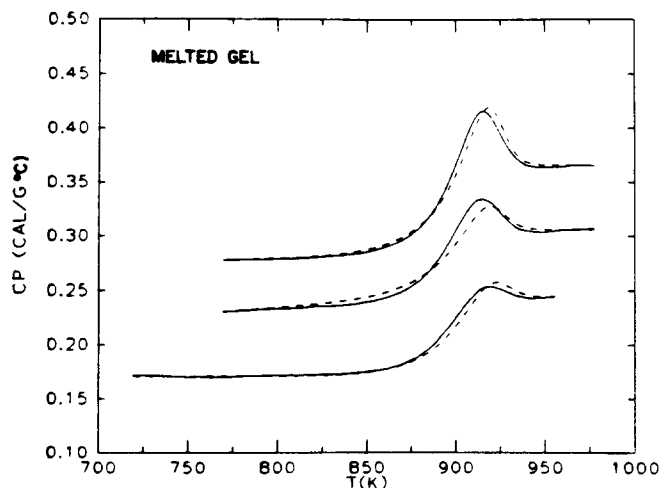


Fig. 3. Same as fig. 2, but with data (solid curves) for melted gel; calculated (dashed) curves based on parameters for desiccated gel.

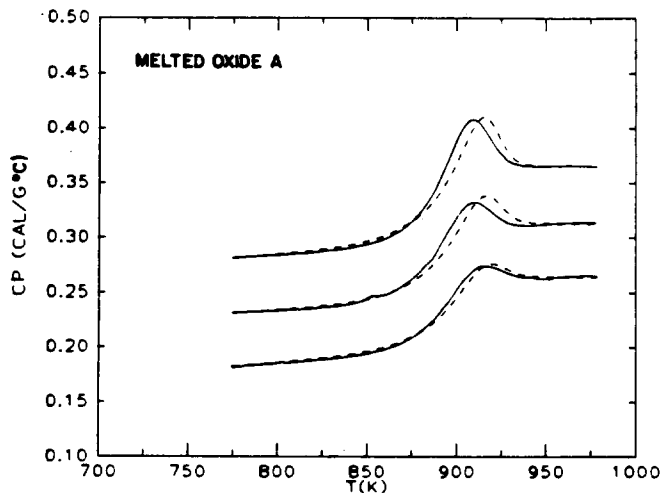


Fig. 4. Same as fig. 2, but with data (solid curves) for melted oxide A; calculated (dashed) curves based on parameters for desiccated gel.

When the sintered gel (2200 ppm OH) is held at 725°C before the DSC scans, a small shoulder occurs $\sim 50^\circ\text{C}$ below the peak in C_p , possibly indicating phase separation. However, no such feature was produced by annealing the desiccated or melted gels, or the melted oxide. Exhaustive TEM examination, after annealing at 725°C, showed no signs of microstructure. Therefore, we believe that the data presented here are for a single-phase glass, and that the unusual fitting parameters do not reflect phase separation.

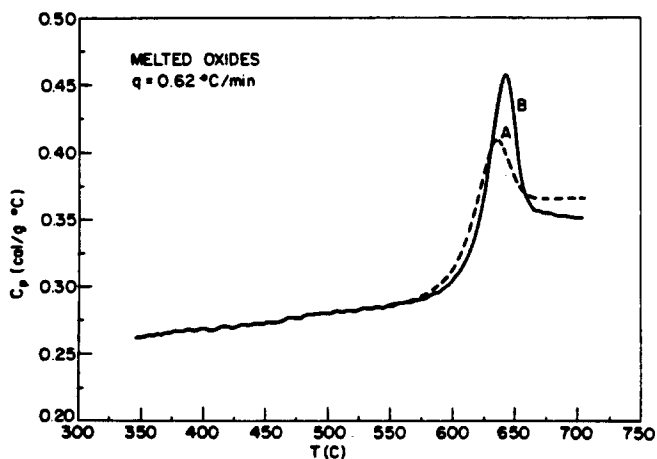


Fig. 5. Reheating curves for melted oxides A and B (see table 1) following cooling at $0.62^\circ\text{C}/\text{min}$.

5. Conclusions

No significant differences could be detected from an examination of the relaxation kinetics of a gel-derived glass and a melted oxide of the same composition and hydroxyl content *.

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* *Note added in proof:* In a paper presented at this conference, Neilson et al. show that there is no difference in the phase separation behavior of a gel-derived glass and melted oxide when the compositions are closely matched. Their previous observation of differences in behavior was apparently caused by small differences in oxide and hydroxyl content (see p. 137).