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Temperature-modulated differential scanning calorimetry analysis of high-temperature silicate glasses

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Recent advances in high-temperature experiments on commercial instruments could enable temperature-modulated differential scanning calorimetry as a method to investigate industrially relevant silicate glasses.

Differential scanning calorimetry (DSC) is one of the most versatile probes for silicate glasses, allowing determination of parameters such as transition temperature (glass, crystallization, or melting) and temperature dependence of heat capacity.[1] However, complications arise for glasses featuring overlapping transitions and low sensitivity, such as SiO_2-rich compositions with small changes in heat capacity during glass transition or low thermocouple sensitivity at high temperature.

These challenges might be overcome using temperature-modulated DSC (TM-DSC), which enables separation of overlapping signals and improved sensitivity at the expense of increased measurement duration.[2] TM-DSC superimposes a sinusoidal heating curve on the linear heating rate from standard DSC, thus providing a temperature (T) profile:

$$T=T_0+\beta t+A\sin(\omega t)$$

where T_0 is initial temperature at time $t = 0$, β is heating rate, A is amplitude of the modulation, and ω is angular frequency of the modulation ($\omega = 2\pi/P$, where P is period).

In the glass science community, TM-DSC has been used to analyze organic, chalcogenide, metallic, and certain oxide glasses. All these glasses have relatively low glass transition temperatures (T_g < 600°C), as this has been the temperature limit of commercially available TM-DSCs—thus excluding the majority of industrially relevant silicate glasses.

Parametric study of TM-DSC for silicate glasses

Recently it has become possible to perform temperature-modulated experiments on commercial instruments at high temperatures (>700°C). However, the transition from low-temperature to high-temperature instruments is not straightforward, as the experimental

parameters used for a typical low-temperature TM-DSC experiment do not directly transfer to those at high-temperature.

Therefore, to obtain good data quality, experimental parameters must be adjusted to fit the probed glass and instrument. The goal when designing experimental TM-DSC parameters is to obtain a linear response between input and output data while achieving a high signal-to-noise ratio (S/N). To elucidate the effect of varying β, A, and P on linearity and S/N, we systematicly studied parametric glass compositions with varying T_g and liquid fragility (m).[3]

We find that for typical high-T_g calcium aluminosilicate glasses (T_g = ~900°C and m = 20–50), β should typically be 2–3 K/min, but for glasses with SiO_2 content of >80 mol.%, β can be as high as 5–7 K/min. A values mainly affect the S/N. On the Netzsch STA 449F1 Jupiter equipment we used, amplitudes of 5 K/min were necessary to achieve adequate S/N. Higher amplitudes might be useful in special cases, such as for pure silica glass with low m, but amplitudes that are too high result in smearing of data and loss of resolution.

Further, Lissajous curves can be used to evaluate if the data exhibit a linear response between heating rate and heat flow, which is required for deconvolution of raw data and is important when studying glass relaxation processes because large enthalpy releases may occur.[4] Data for the high-T_g glasses we studied show linear responses when low heating rates (2–3 K/min) are used in combination with amplitudes that ensure high S/N (Figure 1).

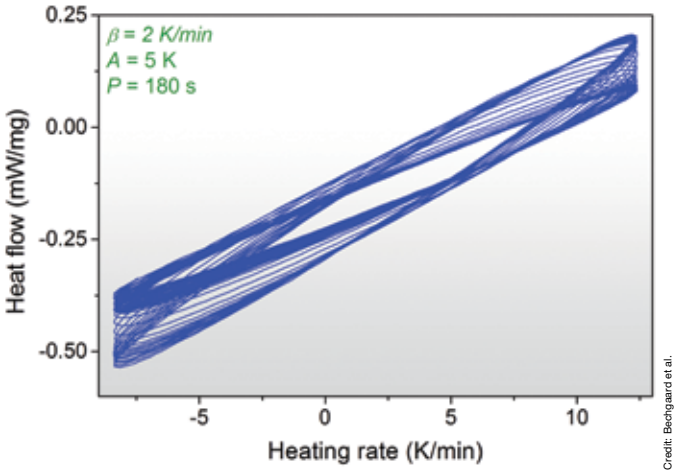

Figure 1. Lissajous curve for a calcium aluminosilicate glass (20% CaO/25% Al_2O_3/55% SiO_2) (β = 2 K/min; A = 5 K; P = 150 s). Data were smoothed slightly using a Savitzky-Golay algorithm[5] and show a linear response.

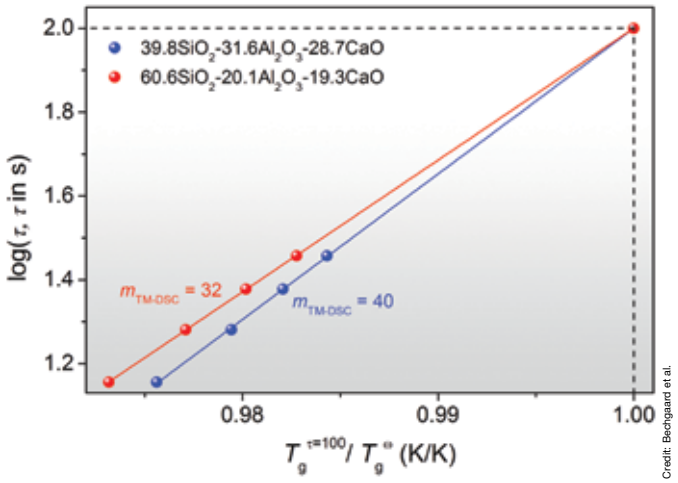

Figure 2. Angell plot of two calcium aluminosilicate glasses, showing relaxation time (τ) slightly above the glass transition temperature (T_g). Relaxation times were determined using $\tau = 1/\omega = P/2\pi$ rad/s. Straight lines represent best linear fit to data.

Liquid fragility determination using TM-DSC

Angell defined the liquid fragility index m as the slope of the logarithmic viscosity (η) versus scaled inverse temperature (T_g/T) curve at T_g:

$$m(x) = \left. \frac{d \log_{10}\eta(T,x)}{d(T_g(x)/T)} \right|_{T=Tg\,(x)}$$

Because the glass transition is a relaxation phenomenon, it also is possible to estimate m from the temperature dependence of structural relaxation time. This has been done for molecular glasses by determining dielectric relaxation time,[6] but it is not possible for silicate glasses because it only relates to polar atomic motions.[7]

Instead, TM-DSC has been proposed as a technique to measure the structural relaxation time of silicate glass-forming systems, using the thermal relaxation caused by temperature modulation.[8]

Deconvolution of raw TM-DSC data allows separation of calorimetric contributions from enthalpy relaxation during the glass transition and heat capacity of the glass itself, identified by imaginary and real heat capacity, respectively.[2] Using the frequency dependence of peak temperature (T_g^{ω}) in the imaginary heat capacity, TM-DSC has already been used to determine fragility of several glass-forming borate melts ($T_g \approx$ 450°C),[9] using a modified Angell plot with relaxation time (τ) instead of viscosity.

A linear relationship between T_g^{ω} and τ at each modulation frequency has been reported,[10] and by extrapolation we can determine the glass transition temperature ($T_g^{\tau = 100}$) where τ = 100 s. By plotting T_g^{ω} reduced by $T_g^{\tau = 100}$ as a function of the τ values at each modulation frequency, we obtain an Angell plot with relaxation time instead of viscosity (Figure 2).

The definition of fragility can then be used to calculate m, as done here for tectosilicate calcium aluminosilicate glasses (Figure 3). From the modulated data, m decreases with increasing silica content, consistent with trends observed from direct viscosity measurements and determined by standard DSC using the activation energy for structural relaxation.[11]

TM-DSC thus succeeds in reproducing the composition-dependent trend in fragility, but absolute values of m are systematically lower for high-m compositions and vice versa for low-m compositions. Additional studies are needed to clarify if this trend generally holds for all silicate glass systems and to make a correction function if necessary.

Detecting silicate glasses with minimal relaxation

TM-DSC has been proposed to be a probe for detecting so-called "intermediate phases," featuring isostatic topology with minimal structural relaxation upon heating.[12] One of the

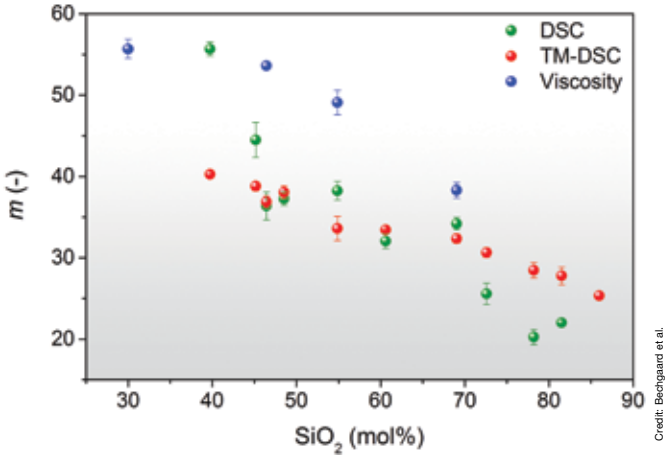

Figure 3. Composition dependence of liquid fragility index (*m*) in fully charge-compensated calcium aluminosilicate glasses. This study determined *m* values by TM-DSC, while we determined *m* using viscometry and Moynihan's DSC procedure in a separate study.[11] TM-DSC captures the compositional trend in fragility.

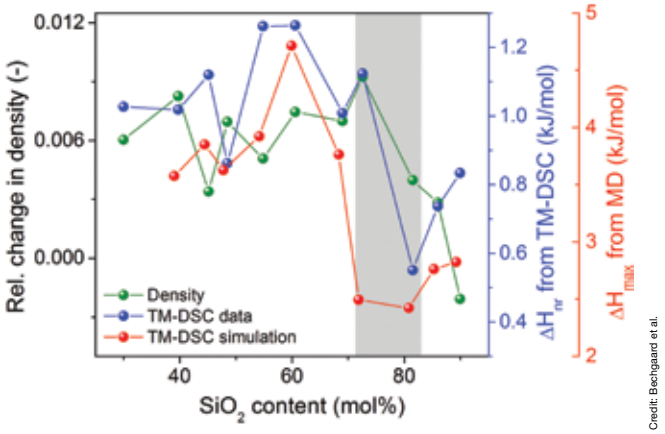

Figure 4. Relative change in density ($\Delta\rho/\rho_0$) in tectosilicate calcium aluminosilicates before and after sub-T_g annealing at $\eta = 10^{15}$ Pa·s (green). Initial density (ρ_0) was measured on samples annealed at $\eta = 10^{12}$ Pa·s (i.e., standard T_g). Compositional dependence of non-reversing heat flow from molecular dynamics (MD) simulations and TM-DSC experiments is also shown (blue and red, respectively). Data suggest that minimum relaxation can be obtained by tailoring the topology of the glassy network.

signatures of glassy materials is a nonequilibrium state that continuously relaxes toward a supercooled liquid metastable equilibrium state. As such, a detailed understanding of the relaxation mechanism is of scientific and industrial interest.

Relaxation-free glasses can be produced by careful design of the glass network topology, but currently known glasses exhibiting these properties are not yet industrially relevant.[13] Therefore, there is interest in identifying industrially useful silicate glasses with minimal structural relaxation for applications such as high-performance displays. This can be achieved by using TM-DSC and identifying a minimum in the non-reversing heat flow, although interpretation of this quantity is still under debate.[14]

Within the fully charge-compensated calcium aluminosilicate system, relaxation behavior can be tuned by changing the network topology, as also confirmed by supplementary molecular dynamics simulations (Figure 4). Further, we studied the magnitude of volume relaxation by annealing at a fixed viscosity. Interestingly, the volume relaxation exhibits minima in the same compositional range as local minima in non-reversing heat flow. Although more work is needed, this suggests that TM-DSC could be used as a tool to search for silicate glasses with minimal volume relaxation during heating.

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Editor's note

Bechgaard will present one of the 2018 Kreidl Award Lectures at the Glass and Optical Materials Division Annual Meeting in San Antonio, Texas, on May 23, 2018.

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