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Parametric study of temperature-modulated differential scanning calorimetry for high-temperature oxide glasses with varying fragility

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ABSTRACT

Differential scanning calorimetry (DSC) has proven to be a highly versatile technique for understanding the glass transition, relaxation, and crystallization behavior of inorganic glasses. However, the approach is challenging when probing glass samples that exhibit overlapping transitions or low sensitivity. To overcome these problems, temperature-modulated DSC (TM-DSC) can be utilized, in which a sinusoidal heating rate is superimposed on the linear heating rate known from standard linear DSC. Until recently, it has only been possible to perform TM-DSC measurements on commercial instruments at temperatures below 973 K, which is insufficient for many oxide glasses of industrial interest, particularly silicate glasses. However, recent commercially available software now enables TM-DSC measurements to be performed at temperatures far exceeding 973 K. To investigate the suitability of using TM-DSC to study glass transition and relaxation behavior in high-temperature silicate systems, we have performed systematic TM-DSC measurements on three different oxide glass systems with varying glass transition temperature and liquid fragility. We find that relatively large underlying heating rates (2–5 K/min) and modulation amplitudes (4–5 K) are needed in order to obtain data with high signal-to-noise ratios. For these combinations of experimental parameters, we also observe a linear response as found using Lissajous curves. Overall, this study suggests that TM-DSC is a promising technique for investigating the dynamics of high-temperature oxide glass systems with a wide range of liquid fragilities.

1. Introduction

Since its invention in 1962 [1], differential scanning calorimetry (DSC) has become an important instrument in the thermal analysis of materials. The technique can be used to identify characteristic temperatures, quantify the heat of thermal events (e.g., phase transitions), and obtain the temperature dependence of the heat capacity [2]. Depending on the calorimeter design, the method can be used to determine heat capacity in the temperature range from 93 to 2673 K, thus covering a diverse range of materials from organic polymers to inorganic crystals and glasses. Due to its versatility, DSC has become a widely used technique for material characterization in research labs and inspection of raw materials or quality control of finished products in industrial facilities [2]. DSC studies have been widely used in the field of glass science to study immiscibility of glass-forming liquids [3], the dependence of the fictive temperature on the thermal history of glass [4–8], glass transition behavior and enthalpy relaxation in hyperquenched glasses [9–11], crystallization behavior and glass stability [12–15], and determination of the fragility index m of glass-forming

liquids [16–19].

Traditionally, DSC has been used to measure heat flow (or heat capacity) as a function of a linear heating profile. As such, the programmed temperature profile (T) can be described as:

$$T = T_0 + \beta t \quad (1)$$

where T_0 is the initial temperature at time $t = 0$ and β is the heating rate. Despite its commercial success, linear DSC suffers from some shortcomings in relation to analyzing certain materials with overlapping transitions. For example, these can be found in composite materials of organic polymers with overlapping glass transitions, but also in single phase materials with imperfect crystals where simultaneous melting and recrystallization occur and in metallic glasses with overlapping glass transition and crystallization processes [20–25]. Linear DSC does not offer the ability to separate such overlapping transitions. Moreover, low sensitivity is a challenge, e.g., when studying glasses with high SiO₂ content that exhibit small changes in heat capacity during the glass transition. In linear calorimeters, the sensitivity can only be improved by increasing sample size and/or heating rate,

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both resulting in decreased resolution due to the larger thermal gradient across the sample and the reduced observation time [26].

To overcome these disadvantages, the temperature-modulated differential scanning calorimeter (TM-DSC) was introduced in 1992 by Reading and co-workers [27–30]. TM-DSC allows for separation of overlapping signals and improved sensitivity at the expense of increased measurement duration [31]. In this approach, a sinusoidal heating rate is superimposed on the linear heating rate, essentially allowing the instrument to use two heating rates. The temperature profile is thus given by

$$T = T_0 + \beta t + A \sin(\omega t) \quad (2)$$

where A is the amplitude of the modulation and ω is the angular frequency of the modulation ($\omega = 2\pi/P$, where P is the period). In modulated DSC, β is the underlying heating rate as the instantaneous heating rate (dT/dt) is now determined by

$$\frac{dT}{dt} = \beta + \omega A \cos(\omega t) \quad (3)$$

The output from a normal linear DSC scan is simply the heat flow signal, while three additional signals, the reversing heat flow, the non-reversing heat flow, and the phase lag, can be obtained by the Fourier transformation of the sinusoidal signals [32,33]. The reversing heat flow describes the temperature dependence of the heat capacity of the sample, while the non-reversing heat flow is related to kinetic events such as relaxation and crystallization. The phase lag describes the time delay between the heat flow signal and the heating rate as a result of thermal inertia of the sample and the instrument. The phase lag is continuous when no transitions occur, but exhibits a peak when the configurational heat capacity of the sample changes. For example, such a phase peak occurs during the glass transition due to the change in configurational entropy [31].

TM-DSC requires three input parameters: average heating rate, oscillation frequency, and the amplitude of the oscillation, complicating the experimental design. Selecting the input parameters can be challenging as the optimal parameters depend on the characteristics of the sample and the investigated phase transition, and changing one parameter affects the most appropriate values of the others. For example, an increase in amplitude requires a decrease in the angular frequency as more time is needed for the heat to flow.

In the glass science community, TM-DSC is currently used to analyze organic, chalcogenide, metallic, and oxide glasses. The applications include easy determination of the glass transition temperature [25,34,35], identifying rigidity transitions [36–39], studying the relaxation behavior during the glass transition [40–46], and determining the liquid fragility index [44–46]. Common to these studies is that the glass transition temperature of the studied samples has been below 973 K. This has been the maximum temperature limit of commercial TM-DSCs, but recently, the TM-DSC technique has become commercially available at temperatures above 973 K. These instruments have a different furnace design than low-temperature (< 973 K) instruments, enabling thermal analysis of, e.g., silicate glasses that exhibit wider glass transitions than any glass measured successfully using a low-temperature TM-DSC [47,48].

The higher operating temperature and wider transitions should require a different set of experimental parameters and result in prolonged measurement time. Therefore, there is an interest in investigating the response of high-temperature silicate glasses to a modulated temperature profile. In this study, we perform systematic TM-DSC experiments on three different glasses to demonstrate how outputs signals are affected as a function of measurement conditions. We choose two calcium aluminosilicate glasses with similar, and relatively high, glass transition temperatures (T_g of 1134 and 1173 K for peraluminous and tectosilicate compositions, respectively), but different liquid fragility indices (m of 48 and 22, respectively). We compare these results with those of a fragile ($m = 82$) [49] sodium borate glass-forming liquid with lower

glass transition temperature ($T_g = 748$ K). Specifically, we perform 80 different heating scans on the peraluminous calcium aluminosilicate composition and 36 scans on both the tectosilicate calcium aluminosilicate and sodium borate compositions. The experimental conditions have been chosen to show the change in response to changes in the β , A , and P parameters.

2. Experimental section

Three glass compositions were prepared by the melt quench method: two calcium aluminosilicates with nominal compositions (mol %) of 55SiO₂-25Al₂O₃-20CaO (CAS1) and 86SiO₂-7Al₂O₃-7CaO (CAS2) and one sodium borate glass with nominal composition 67B₂O₃-33Na₂O (NaB). Both the CAS1 and CAS2 glasses exhibit relatively high glass transition temperatures of 1134 and 1173 K, respectively [50], as determined using a 10 K/min heating rate on a standard DSC. The peraluminous CAS1 composition exhibits relatively high fragility index ($m = 48$), while the tectosilicate CAS2 composition is relatively strong ($m < 22$) [50]. NaB exhibits a much lower glass transition temperature of 748 K, but higher fragility index of 82.1 [49].

To obtain homogenous glasses, the raw materials (analytical grade SiO₂, Al₂O₃, CaCO₃, H₃BO₃, and Na₂O powders with purity > 99.8%) were mixed for 60 min in a ball mill before being melted in air for at least 6 h at 1923 K for CAS glasses and 1373 K for NaB and then quenched. The calcium aluminosilicate glasses were re-melted overnight at 1923 K in air and quenched on a metal plate. All glasses were annealed at their respective T_g for 30 min.

The calorimetric measurements were performed on a Netzsch STA 449F1 Jupiter® calorimeter with the TM-DSC module software extension in Pt-Rh crucibles using argon as the purge gas (flow rate = 50 mL/min). The samples were disc-shaped with a diameter of ~6 mm and thickness of ~0.4 mm, resulting in a mass of ~30 mg. To ensure an optimal heat transfer between sample carrier and samples, the samples were polished to an optical finish on the surface facing the crucible bottom. To evaluate the effect of the three modulation parameters on the calorimetric data, the glasses were scanned using a combination of parameters resulting in a total of 80 scans for CAS1 and 36 for both CAS2 and NaB. For CAS1, the experimental conditions included $\beta = 2, 3, 4, \text{ and } 5$ K/min, $A = 1, 2, 3, 4, \text{ and } 5$ K, and $P = 90, 120, 150, \text{ and } 180$ s. CAS2 was scanned with $\beta = 3, 5, \text{ and } 7$ K/min, $A = 3, 5, \text{ and } 7$ K, and $P = 90, 120, 150, \text{ and } 180$ s, while NaB was scanned with $\beta = 2, 3, \text{ and } 4$ K/min, $A = 1, 3, \text{ and } 5$ K, and $P = 90, 120, 150, \text{ and } 180$ s.

The modulated scans were performed between 1023 and 1238 K, 1053 and 1318 K, and 703 and 793 K for CAS1, CAS2 and NaB, respectively. This was done to cover a wide enough temperature range from the glass to the supercooled liquid. The low temperature limit in the glass corresponds to an average relaxation time, which is much longer than the period of the oscillation. The high temperature limit in the liquid corresponds to an average relaxation time, which is much shorter than the period of oscillation, assuring that no crystallization occurs during the measurement. All upscans were performed subsequent to a linear cooling segment (downscan) with the same β as the subsequent upscan. For example, the temperature profile could be cooling from 1238 to 1023 K with $\beta = -2$ K/min, followed by heating from 1023 to 1238 K with $\beta = 2$ K/min, $A = 5$ K, and $P = 150$ s. To ensure identical heat transfer, all scans on each glass were performed without opening the furnace tower and thus touching the sample carrier. The phase angle and reversing and non-reversing heat flows were obtained from TM-DSC signals and presented herein without any post corrections. To test the reproducibility of the TM-DSC data, we performed repeated scans for selected experimental conditions on the same sample. The difference in peak position values was always within ± 1 K.

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