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Solids

## Heating rate effect on the activation of viscoelastic relaxation in silicate glasses

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### Abstract

Here we present a direct investigation of the heating rate effect on structural relaxation of sodium silicate glass near the glass transition by means of differential scanning calorimetry, and show the sensitivity of Brillouin light spectroscopy to the dynamic of structural relaxation in the medium range order (~100 nm).

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### Introduction

Glass is one of the earliest man-made materials. It is ubiquitous in nature and technology. Window glass, composed mostly of sand, lime and soda, is the best-known example of an engineered amorphous solid. It entails supercooling of a liquid to fail attaining a metastable equilibrium and taking advantage of viscous

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retardation of nucleation and crystallization during the time scale of the fabrication [1]. Upon cooling, molecular motion slows down and eventually molecules will rearrange so slowly that they cannot adequately sample configurations in the available time allowed by the cooling rate. The liquid's structure therefore appears 'frozen' on the laboratory timescale (for example, minutes) and shows an excess energy with respect to the reference crystalline state [1-5]. This excess energy constitutes the thermodynamic driving force for spontaneous structural rearrangements generally referred to as structural relaxation. Structural relaxation takes place when the glass is cooled, heated, or kept at a finite temperature in the vicinity of  $T_g$  [5-10]. This later process has been studied extensively in glasses and polymer glasses where it is referred to as "annealing" or "aging" and here it is of great interest for the understanding the nature of the glass transition [9-11]. In literature most of the experiments probing structural relaxation typically involve creating an unstable, non-equilibrium state through a rapid temperature jump from above  $T_g$ , and then following the relaxation to a metastable equilibrium by monitoring some glass properties [12-15]. Usually, the initial non-equilibrium state is sufficiently far from equilibrium, with the consequence that the average time scale for reaching a metastable equilibrium can be quite different from the average time scale for linear response dynamics in the final metastable equilibrium state (for simplicity we will refer to the metastable phase as an equilibrium phase). In addition, it has been observed that relaxation function describing the relaxation profile of a probed glass's property, usually follows a non-exponential law generally described by the Kohlraush-William-Watts function  $(\exp(-\frac{t}{\tau})^\beta)$  [3]. This is because either individual relaxation time is intrinsically nonexponential or the actual transformation is made-up of many mechanisms of different relaxation times. Many experimental and theoretical works have been devoted to shed some light on the microscopic origin of this heterogeneous dynamics [16-19]. The resulting picture is that this distribution of relaxation time scales is related to spatial heterogeneities that might exist in the liquid and been frozen in below the glass transition  $T_g$ .

The presence of the mentioned heterogeneous relaxation is the typical behavior found in the so-called "fragile" glass forming-liquids, which include polymers and most of molecular glass-formers, and the results discussed so far concern only these systems, where dynamics of all atomic species do not occur at the same time scale. There is, however, a weak knowledge on the dynamics of the so-called "strong" glass-forming liquids, such as sodium-silicates glasses, where sodium ( $\text{Na}^+$ ) ions move on a time scale that, at temperatures in the vicinity of  $T_g$  is many orders of magnitude faster than the one of atoms constituting the matrix (Si and O). We have shown in a recent study of structural relaxation dynamics in a sodium silicate glass that relaxation are heterogeneous at the intermediate length scale whereas they are indeed homogenous at the interatomic length scale [20]. In this former study, relaxation dynamics was studied during annealing, by a fast jump from below the glass transition to the annealing temperature. In the present study, we shed some light on the heating rate effect on structural relaxation of sodium silicate glass near the glass transition by means of Differential scanning calorimetry (DSC) and highlight the dynamic of structural relaxation in the medium range order by Brillouin Light spectroscopy (BLS). This study will be described in details in a following publication [21].

## Materials and methods

### *Sample preparation*

Ingots of sodium silicate glass with 27% mole was synthesized using  $\text{SiO}_2$ (99.9%) , and  $\text{Na}_2\text{CO}_3$ (99.9%) in the right proportions as the starting materials. 100g of the prepared powder was intimately mixed, then heated and melted in a Pt-Rh crucible at 1900K for a period of time sufficiently long (4 hours) to eliminate all gas bubbles from the melt and to achieve homogeneity, the melt was then poured into a stainless-steel mold kept at room temperature. The ingot of glass was cut by a diamond saw into  $\sim 2 \times 2 \times 1 \text{mm}^3$  parallelepipeds and optically polished.

### Differential scanning calorimetry (DSC):

The heat capacity was measured with a differential scanning calorimeter (Setaram DSC MHTC 96). Before each measurement, an empty platinum crucible was heated and cooled to measure the baseline, and a calibration measurement was performed with a crucible containing 200 mg of sapphire. 200 mg of glass finely grounded in a mortar was placed in a platinum crucible. The glass sample was first heated to 200 °C for 10 min then to 800 °C with different heating rates 10 and 25 °C/min.

### Brillouin light spectroscopy (BLS):

Brillouin spectra were recorded in a back-scattering geometry ( $\theta=180^\circ$ ). The incident light was produced by an argon ion laser equipped with an internal etalon in order to promote the lasing of a single longitudinal mode at wavelength of 514.5 nm. The scattered light was analyzed using a six-pass tandem Fabry-Perot interferometer (JRS) [22]. The intensity of the filtered light was measured with a Thorne EMI photomultiplier tube, and recorded on 1024-channel multichannel analyzer. The heating system is achieved using a TS1500 Linkam device (Tadworth,U.K). The sample is placed inside a ceramic sample cup (~ 1mm deep) where a ceramic heat shield is placed over the top to prevent heat escaping this micro oven, so the sample is heated from underneath as well as from the sides, ensuring good temperature homogeneity. The laser beam was positioned to enter and exit the ceramic sample cup through a small hole in the top and the bottom, permitting the un-scattered light to leave the sample chamber. The temperature is accurately controlled by a system controller, which enables the stage to heat the sample at different heating rate to the chosen temperature.

## Results and discussion

Differential scanning calorimetry (DSC) monitors the heat absorbed or evolved by a material as a function of time, during rate heating. DSC is used to characterize the kinetics of structural relaxation as well as the study of temperature dependence of the relaxation times controlling the structural relaxation and viscous flow processes associated with the glass transition.

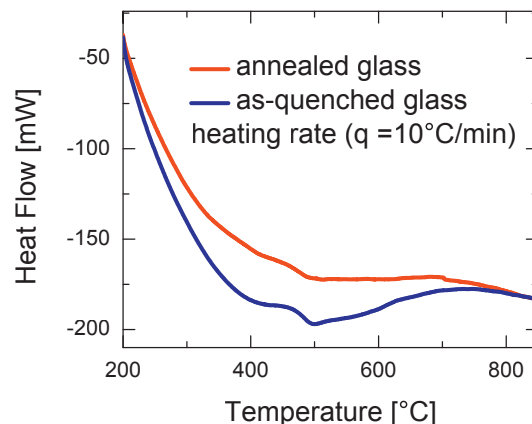


Figure. 1: Heat flow curves measured by DSC for an as-quenched and an annealed glass sample during heating with a rate of 10°C/min.

Figure 1 shows the heat flow as a function of temperature for an as-quenched glass (without further heat treatment) and an annealed glass (annealing was achieved by keeping the glass at a temperature of at 510°C for 5 hours then cooled to room temperature). From figure 1 one could notice that the glass transition shift to

low temperatures upon annealing ( $T_g(\text{as-quenched}) = 502 \text{ }^\circ\text{C}$  and  $T_g(\text{annealed}) = 479 \text{ }^\circ\text{C}$ ).

Figure 2 shows the heat capacity ( $C_p$ ) curves as a function of temperature for an as-quenched glass samples heated with different heating rate  $q = dT/dt$ . Heating at a rate  $q$  can be thought of as a series of small temperature steps  $\Delta t = \Delta T/q$ . Below  $T_g$ , the relaxation time  $\tau$  is very long compared to  $\Delta t$ . The temperature dependence of  $\tau$  is well described by the Tool-Narayanaswamy equation [5]:

$$\frac{d \ln \tau}{d\left(\frac{1}{T}\right)} = \frac{\Delta H^*}{R} \quad (1)$$

Same behavior observed on heat flow changes as a function of temperature has been observed on  $C_p$  curves, upon decreasing the heating rate, the location glass transition  $T_g$  in  $C_p$  curves shift to low temperatures. When decreasing the heating rate  $q$ , the characteristic time scale  $\Delta t$  will increase, and since the relaxation time increase with temperature, this will shift the glass transition to lower temperatures.

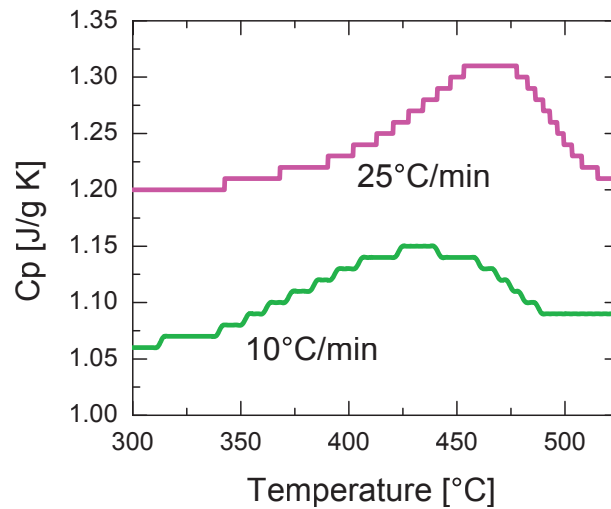


Figure. 2: Heat capacity curves for an as-quenched glass measured by DSC during heating through the glass transition region at two different rates.

Brillouin light scattering spectroscopy has been used to investigate the structural relaxation through the investigation of the viscoelastic properties of the medium. Here an as-quenched glass was heated at a fixed temperature near the glass transition, and kept at this temperature for about 3 days. During isothermal heating, Brillouin spectra were recorded as a function of time. All the spectra acquisition consists of 500 cycles (5min acquisition time) and waiting time of 3s between spectra. This allows acquiring a large number of spectra for data recordings, which can reach 1000 spectra, allowing very good statistics and high sensitivity to weak variations. The line shape analysis of the Brillouin spectra reveals information about the mechanical rigidity and viscous dissipation in the scattering medium. Like any other probe, typical phonon frequencies in this experiment are in the vicinity of  $10^{10}$  Hz, and it is found to probe the structural integrity on the scale of 100 nm [23].

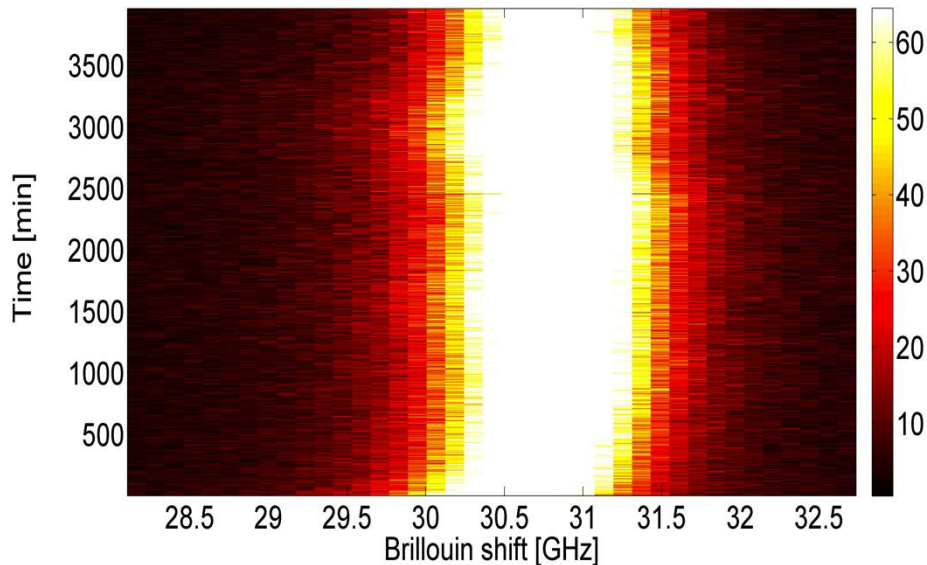


Figure. 3: Time-Brillouin shift 2D image of the sample heated at 413 °C for about 72 hours. . The x -axis is the Brillouin shift, the y-axis is the annealing time and the color scale shows the Brillouin intensity.

Figure 3 shows a 2D image contour plot of the Brillouin spectra as a function of the annealing time. The x -axis is the Brillouin shift, the y-axis is the annealing time and the color scale shows the Brillouin intensity. One can see that when heating isothermally the glass sample at a fixed temperature the Brillouin frequency shift toward higher frequencies until it reach a plateau after about 24 hours. By fitting the relaxation profile of the Brillouin frequency as a function of annealing time we reveal the existence of two-relaxation process: (i) fast (ii) slow dynamics. A fast with an apparent relaxation time  $\tau_1 = 2$  hours and  $\tau_2 = 20$  hours [20].

As discussed above Brillouin spectroscopy provides information on the dynamics of structural relaxation over length scales where the density and composition fluctuations present in the liquid are frozen in around the glass transition. During aging each of these frozen-in regions should result in distinct aging rates, then a dynamic heterogeneity is observed. In this case the non-exponential arises from a sum of exponential relaxation each with a characteristic barrier height and time constant. In the super-ionic this glass system Na<sub>2</sub>O-SiO<sub>2</sub> with 27% Na<sub>2</sub>O, it has been shown that sodium ions hop from site to site along conducting pathways in the Si—O matrix. As a consequence, one can imagine at least two different sets of environment, namely unconstrained silicate tetrahedra close to the pathways of Na ions (in the boundaries of silicate Si--O chain), thus relaxing in fast timescale followed by a slow silicate Si--O chain (intervening Si--O--Si bond angles) motion giving rise to a very slow cooperative relaxation.

Having discussed the possible scenario of the observed heterogeneous dynamics, we now turn our attention to the heating rate effect on the activation of the structural relaxation. One of the main results is that at heating rate  $q$  sufficiently high (25 K/min), the relaxation time seems to be smaller as shown from  $C_p(T)$  curves than heating with a very slow  $q$ . One can assume that motions of non-constrained SiO<sub>4</sub> tetrahedra, i.e. that presents a high degree of freedom is the case on the basis of the fast relaxation. This is followed by a slow cooperative motion of SiO<sub>4</sub> tetrahedra though to involve configurational rearrangement of the glass structure. Structural relaxation studies of K<sub>2</sub>O-SiO<sub>2</sub> (29% K<sub>2</sub>O) probed in the short-range order by Raman spectroscopy have shown that SiO<sub>4/2</sub> structural units relax in a time scale in the order of an hour [24]. As one can see, this is in good agreement of our fast relaxation time. Furthermore, as the relaxation time scale decrease upon

decreasing the heating rate suggests that the characteristic length scale of these regions is reduced as consequence of the decrease in the average size of these regions. This indicates that structural relaxation dynamics is controlled by the cooperative rearrangements of the structure as explained by Adam-Gibbs [25, 26], and the measured time scale for structural relaxation depends on the probability of the system to rearrange.

## Conclusion

We have shown from DSC measurements that the heating rate is strongly correlated to structural relaxation below  $T_g$ , and to activation energy through the Tool- Narayanaswamy model. We showed the sensitivity of Brillouin Light spectroscopy to structural relaxation on the 100nm length scale, and we gave an approximation of the relaxation time of about 20 hours at the investigated temperature.

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