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Influence of thermal history on the structure and properties of silicate glasses

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Abstract

We studied a set of float glass samples prepared with different fictive temperature by previous annealing around the glass transition temperature. We compared the results to previous measurements on a series of amorphous silica samples, also prepared with different fictive temperature. We showed that the modifications on the structure at a local scale are very small, the changes of physical properties are moderate but the changes on density fluctuations at a nanometer scale are rather large: 12 and 20% in float glass and silica, for relative changes of fictive temperature equal to 13 and 25% respectively. Local order and mechanical properties of silica vary in the opposite way compared to float glass (anomalous behavior) but the density fluctuations in both glasses increase with temperature and fictive temperature.

Key words: fictive temperature F125, silica S160, float glass F 145
PACS: 61.43.Fs, 61.10.Eq, 78.30.-j, 78.35.+c

1 Introduction

The structure and formation of glass, though being studied for decades, are still puzzling problems. Liquids quenched with different cooling rate, or having different thermal histories, provide glasses with different structures and properties [1]. The local structure of silicate glasses is rather well-known: the "building units" are similar to that of the crystalline counterparts (SiO_4 tetrahedra), but at intermediate range the tetrahedra are linked together in a disordered fashion with a bound angle distribution, which has been shown to

depend on thermal history in silica [2]. Modifiers, such as alkaline species, induce breaking of intertetrahedral bounds. This phenomenon is often referred to as "depolymerization" of the glassy network. No much is known about the structure at larger scale. However density and concentration fluctuations present in the liquid are expected to take place at the nanometer scale and to be partly frozen-in around the glass transition.

In order to determine the structural changes on different length scales and how the macroscopic properties are affected by thermal history, we had studied silica samples (glass transition $T_g = 1260$ °C) prepared with well defined thermal history [3,4,5,6,7]. In this paper, we present new results about a commercial "float" glass ($T_g = 560$ °C), very widespread because used as window glass. Both composition are examples of usual silicate glasses, among the most technologically important. All samples have well characterized thermal histories, prepared by thermal annealing at different temperatures in the glass transition range and then quenching on a metallic plate. Samples prepared this way keep the structural organization present in the liquid at the temperature at which the structure is frozen-in. This temperature, called fictive temperature, T_f, [1], can be used as a characteristic of the simple thermal histories (stabilization and quenching) performed in this work. The fictive temperature of the samples is equal to the annealing temperature if the annealing time is long enough to stabilize the structure and properties (longer than the relaxation time for viscosity, $\frac{\eta}{G_\infty}$, where η is the viscosity and G_∞ the infinite frequency shear modulus) and the quench fast enough to retain its configuration.

2 Experimental Procedure

The commercial "float" glass, of composition 72% SiO_2, 14% Na_2O, 9% CaO, 3% MgO, 1% Al_2O_3 plus other minor oxides, is provided by Saint-Gobain Recherche, Aubervilliers, France. Four heat treatments have been performed, in order to prepare samples with fictive temperature T_f ranging from 480 °C to 620 °C annealing. The annealing times range from 2h for 620 °C to 16 weeks for 480 °C. They were estimated from the stabilization time for silica glass as equivalent viscosity. Moreover, we also measured the SAXS signal on a series of samples annealed for different times at 480 °C and also during some in situ annealing, in order to check that stabilization was reached. It should be noted that temperature dependent SAXS measurements on synchrotron were performed on a 12 week annealed sample but the results showed that this time was insufficient, and thus 16 week treatment were performed later. The results are compared to measurement in a very high purity (low OH content) type I [8] silica glass. The heat treatments performed to prepare different samples with different thermal histories, corresponding to fictive temperatures, T_f, ranging from 1100 °C to 1500 °C have been described previously [4,6,9]. For

silica, the spectroscopic measurements yield a method to check that the fictive temperature is most probably equal to the annealing temperature.

The local structure is probed using in situ Raman spectroscopy as a function of temperature for float glass, with an incident wavelength $\lambda = 5145$ Å, using a Jobin-Yvon T64000 set-up. Raman room temperature measurements for silica have been reported before [3,10]. Larger scale structure fluctuations at the nanometer scale) is investigated up to 700 °C (1500 °C for silica) using Small Angle X-ray Scattering (SAXS) on D2AM instrument at ESRF (Grenoble, France), with an incident energy E=18keV, using a molybdenum furnace [11]. Finally, we determined temperature dependent macroscopic longitudinal sound velocity (or modulus), using Brillouin scattering ($\lambda = 5145$ Å) performed with a high resolution spectrometer [12,13] in backscattering geometry. All the optical temperature dependent measurements where achieved using a Linkam TS1500 device.

3 Results

Results about silica have been described before and we will first present data obtained in float glass. Raman spectra of float glass (Insert of Fig. 1) exhibit two main features: a broad peak around 600 cm^{-1}, and a line around 1100 cm^{-1}. The position of the Raman line around 1100 cm^{-1} is shifted to lower frequency when the temperature increases (Fig. 1a), with a change of slope at the glass transition (around 560 °C). At room temperature, the line around 1100 cm^{-1} is shifted down by about 3 cm^{-1} *i.e.* 0.3% for a fictive temperature change, $\Delta T_f/T_f = 17\%$ (Fig 1b). We also observed around the glass transition, a (rather small) relaxation of the sample stabilized at 620 °C (Fig. 1a). The position of the 1100 cm^{-1} line evolves toward that of the sample of lowest fictive temperature as the relaxation time of this sample is shorter than the measuring time (10 min): the sample lowers its T_f during the measurements.

The amplitude of the density (concentration) fluctuations can be deduced from the SAXS spectra by extrapolating to q=0 the signal just below the first diffraction peak (observed around $q = 1.5$ Å^{-1} for float glass) (Fig. 2a). Like in silica glass [6], we observe a rather large influence of T_f on the amplitude of fluctuations at room temperature (Fig. 2b). The sample treated 12 weeks at $T_f = 480$°C is probably not fully stabilized. Thus the fictive temperature range to consider for those SAXS measurements is only 510-620 °C. The SAXS intensity vary then by about 12% for a fictive temperature change of 13%. We observe, like for the Raman shift, a clear relaxation in the glass transition region for the sample with the highest fictive temperature. On the other hand for the two samples treated at the lowest temperatures (480 and 510 °C), we

observe a "delay" to reach the supercooled liquid curve when heating, due to relaxation times longer than typical experimental times.

Finally, the influence of temperature (Fig. 3a) and fictive temperature (Fig. 3b) on sound velocity of float glass has been measured by Brillouin scattering. The effect is very similar to that on the SAXS intensity $I(q = 0)$ except that the sound velocity decreases when both T and T_f increases. The sample stabilized at 480 °C has been heat-treated 16 weeks (as for Raman measurements) and can be considered as fully stabilized. We observed the influence of fictive temperature in the glassy state (a variation of 2.45% for a fictive temperature change of 16%) as well as a relaxation effect around the glass transition for the samples of $T_f = 620$ and 590 °C. A "delay" effect can be noticed for $T_f = 480$ and 510 °C. The changes are clearly much lower on the sound velocity than on the SAXS intensity.

In silica, vibrational spectroscopy measurements showed that when T_f increases, the frequency of the main band at 440 cm^{-1}, related to symmetric $\widehat{\text{Si-O-Si}}$ bend increases by 2%. [5]. The area of defect lines (at 480 and 520 cm^{-1}) also increases with increasing T_f. On the other hand, the changes on the amplitude of density fluctuations, $I(q = 0)$, have been reported to be very large below the glass transition, about 20% at room temperature for a $\Delta T_f/T_f$=25% [6,9]. A structural relaxation effect (decrease of $I(q = 0)$ for high T_f) has also been observed in the glass transition range [6]. In situ isothermal relaxation can also be observed as a function of time (fig. 4). A typical relaxation time for as-received sample annealed at 1175 ° C is about 40 min, comparable to the evolution time observed by Raman and infrared spectroscopies for samples annealed for different times at a given temperature (30 to 70 min) [14]. The sound velocity vs temperature curves in silica, deduced from Brillouin scattering, are very different from that of float glass: the sound velocity increases with temperature, and no change of slope is observed at the glass transition [7]. The influence of fictive temperature in silica is very small, the sample of lower fictive temperature being softer (having a lower sound velocity) by 0.2% for $\Delta T_f = 25\%$ [7].

4 Discussion

The changes of Raman spectra in silica with T_f can be interpreted as a decrease of the average angle $\widehat{\text{Si-O-Si}}$ [2,15,16,5], and thus as a local densification. On the other hand the change on amplitude of the so-called defect lines as a function of T_f also indicates that either the number of small cycles, involving 3 to 4 SiO_4 tetrahedra, increases with T_f, either those cycles are more decoupled from the other vibrations. The first hypothesis also implies local densification

and decrease of $\widehat{\text{Si-O-Si}}$ angle ($d\theta/dT_f = -0.00623°/°C$) [2]. In Raman spectra of sodium silicate glasses, the feature at 1100 cm^{-1} is attributed to vibrations of different Q_n species with a main contribution from Q_3, a low frequency side due to Q_2 and a high frequency side due to Q_4 [17] (Q_n is a SiO_4 tetrahedron linked to n other tetrahedra toward n bridging oxygens). The Raman spectra of float glass being very similar to that of sodium silicate glass, we infer that a shift downward can be interpreted as an increase of the Q_2 population. This result is in agreement with a local depolymerization of the silicate network with increasing fictive temperature, also observed by RMN in soda-lime silicate glass [18]. Almost no study of the influence of the heat-treatment on the Raman spectra of float glass or other silicate glass can be found in the literature [19]. Few studies of the influence of T_f have been carried out by infrared spectrometry in float glass [15] and in a lithium aluminosilicate glass [20]. The changes induced in the infrared spectrum by modifying T_f are difficult to observe due to broad features in the spectra. The frequency changes in float glass is in opposite sense compared to what is observed in infrared spectra of silica. Surprisingly, in the aluminosilicate glass with 70% of SiO_2, 15%Al_2O_3, 15%Li_2O, the frequency of infrared feature at 1080 cm^{-1} varies in the same way as it does in silica [20], thus showing the complexity of behavior in silicate glass, probably due to several contributions being mixed in one single peak. The Raman spectra are also difficult to interpret in aluminosilicate glasses because of the interplay of several contributions (for example modes involving Si and Al are expected to have very similar frequencies) which may vary in opposite sense.

For both silica and float glasses, a T_f increase induces a rather noticeable increase of the amplitude of density fluctuations. Moreover the evolution with temperature is similar for silica glass and float glass: an increase of $I(q = 0)$ with temperature and a change of slope, toward larger slope at the glass transition. The amplitude of density fluctuation is larger in silica, frozen-in at high temperature, than in float glass. The ratio of extrapolated scattered intensity, respectively around 22 and 12 e.u/molecules for silica and float glass, is roughly equal to the ratio of glass transition temperatures : 1533 and 833 K. It can be noted also that the observation of the relaxation around the glass transition in silica glass is a rather new result. Indeed, such relaxation effect is usually observed in silicates glasses by dilatometry measurements or differential scanning calorimetry. However, in silica both kinds of measurements are difficult due to the high T_g and also to the low thermal expansion of silica.

The sound velocity vary in the opposite way for silica and float glass, and the influence of T_f is very low (0.4%) in silica. Both effects are due to the elastic anomaly of silica.

5 Conclusion

For both silica and float glass samples, we observed that the modifications induced on the local order, by changes of the fictive temperature, as probed by spectroscopic methods are small. A noticeable influence of fictive temperature is observed on the macroscopic elastic modulus of float glass. In silica, the influence of T_f on elastic modulus is small and is in opposite sense compared to float glass due to the inelastic property anomalies of silica. SAXS measurements show that, for both glasses, the higher fictive temperature contains fluctuations of larger amplitude, and the effect is rather important: changes of more than 10% in the SAXS intensity are observed for fictive temperature changes of the same order. This result could be considered as rather intuitive but does not correspond to previous observation in amorphous polymers where the effect of thermal history is hardly observed [21,22].

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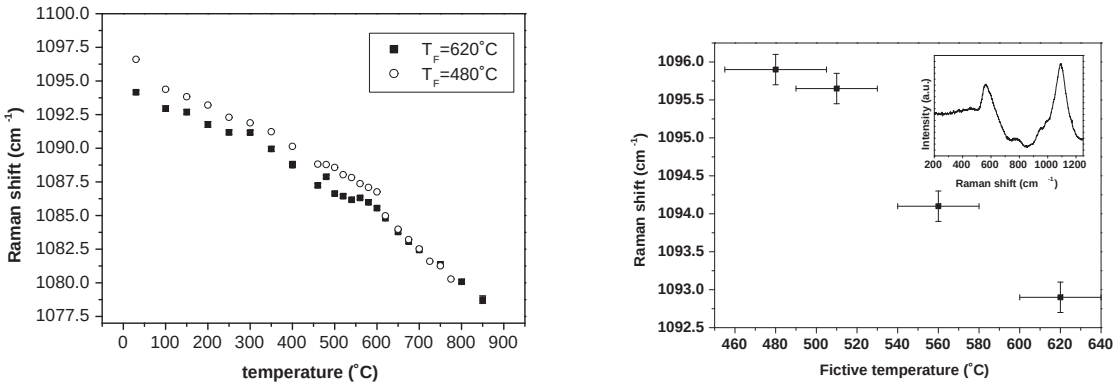
Fig. 1. a) (left) Evolution with temperature of the Raman line around 1100 cm^{-1}, for two samples corresponding to fictive temperatures 480 and 620° C, respectively. b)(right) Position of the line around 1100 cm^{-1} at room temperature as a function of T_f. Insert: Example of Raman spectra in float glass

Fig. 2. a)SAXS extrapolated intensity as a function of temperature for 4 float glasses with different heat treatment. The sample annealed 12 week at 480 °C is not fully stabilized. The error on $I(q = 0)$ is $\pm 2\%$ b) I(q=0) at room temperature as a function of T_f for the same samples.

Fig. 3. a) Sound velocity as a function of temperature for 6 float glass samples prepared with different fictive temperatures. b) Brillouin shift (proportional to sound velocity) at room temperature as a function of T_f. The error bar on sound velocity are 0.1 %.

Fig. 4. Evolution of $I(q = 0)$, with time during annealing . Insert: $I(q = 0)$, as a function of temperature for as-received sample during temperature dependent measurements (crosses), for as received sample during annealing at 1175 °C (triangles), and for sample of $T_f = 1200$ °C (circles). The error on $I(q = 0)$ is $\pm 2\%$

Figure captions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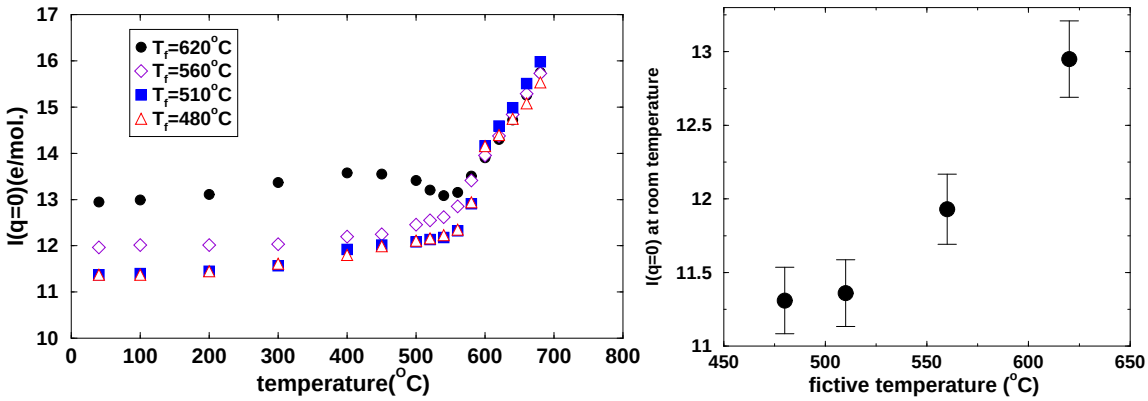
temperature (˚C)
T_F=620˚C
T_F=480˚C
Fictive temperature (˚C)
Intensity (a.u.)
Raman shift (cm -1)

Fig. 1


I(q=0)(e/mol.)
temperature(°C)
T_f=620°C
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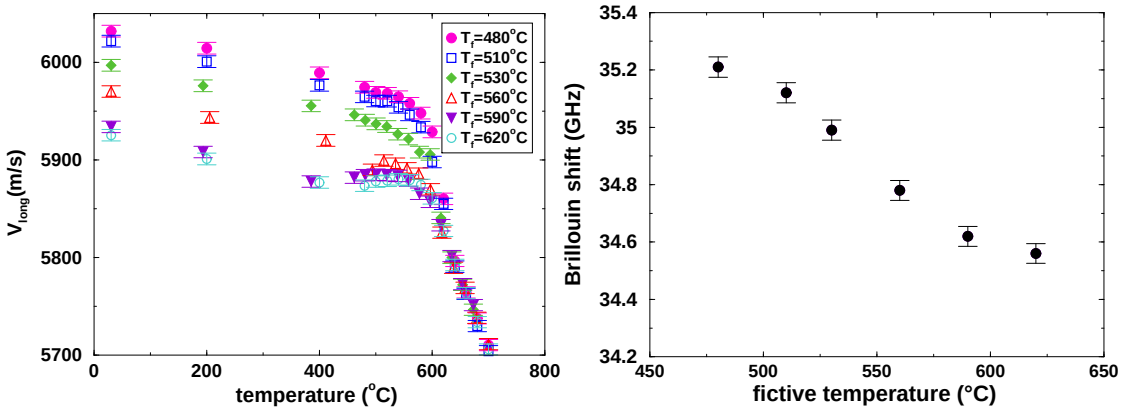
T_f=510°C
T_f=480°C
I(q=0) at room temperature
fictive temperature (°C)

Fig. 2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T_f=530°C
T_f=560°C
T_f=590°C
T_f=620°C
V_{long}(m/s)
temperature (°C)
Brillouin shift (GHz)
fictive temperature (°C)

Fig. 3

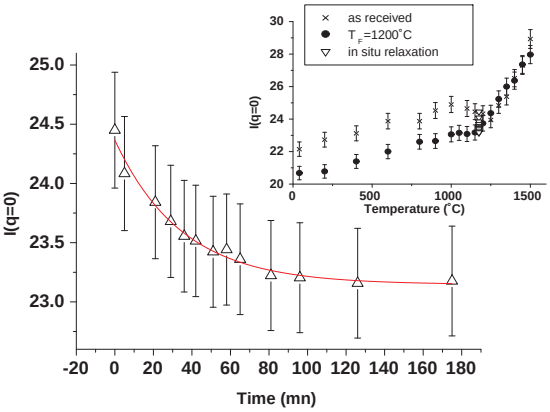
as received
T F =1200°C
in situ relaxation
I(q=0)
Temperature (°C)
I(q=0)
Time (mn)

Fig. 4