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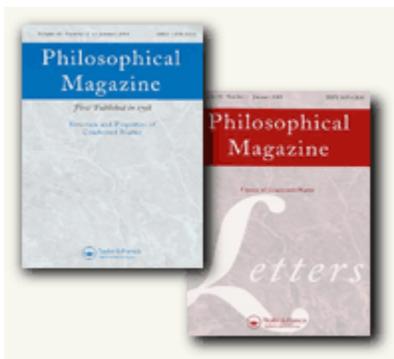
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Density and density fluctuations anomalies of SiO₂ glass: comparison and light scattering study

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Abstract

The objective of this work is to compare density and density fluctuations of silica as function of temperature in the anomalous domain between 950°C and 1480°C by comparing Archimedes' macroscopic measurements and light scattering. A parallel qualitative behaviour is observed between density fluctuations and macroscopic density. Density fluctuations of silica show a minimum as function of the temperature as the macroscopic density does: this correlation indicate a possible common origin of both observations.

1. Introduction

Silica glass is, both theoretically and experimentally, one of the more studied materials. Its technological importance has not to be demonstrated and it is in principle one of the simplest single component glass. However, as for water [1-2], some of its basic properties, density and sound velocity temperature dependence are still unexplained [3-4]. The evolution, of the density with the fictive temperature above 1100°C is one of the anomaly of silica described a long time ago [5]: although in most materials the density decreases with the increase of the temperature, SiO₂ density increases with temperature from 1100°C up to a maximum near 1550°C and decreases for higher temperatures, the position of this maximum being strongly dependent on the amount of the different OH groups or Al, Na or Cl impurities. Molecular dynamics simulations [6] have described the increase of the density with temperature on the basis of a polymorphism of silica. Recent experiments [7] in the temperature region between 600° and 1000°C demonstrated further the occurrence of a minimum in the density versus the temperature at approximately 950°C. However the difficulty of these studies results from the very high viscosity of the silica glass below the glass transition temperature T_g : the interpretation of an experiment at a temperature T must include both the influence of the anharmonicity corresponding to the actual temperature of the experiment and the effects due to the freezing of the structure at

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a fictive temperature T_f : this corresponds to the interpretation of experiments in a non equilibrium state [8].

In this paper, we will discuss the light scattering studies performed at room temperature of a pure silica glass heat-treated in the temperature range 950°C – 1450°C in order to compare density and density fluctuations. We will consider silica samples with different fictive temperatures T_f , defined as the temperature at which the glass would be in internal equilibrium i.e. temperature at which the liquid is frozen in. This fictive temperature can be changed by a thermal annealing long enough to achieve the thermal equilibrium followed by a quenching at room temperature. Fictive temperature T_f of a given sample will be determined from spectroscopic Raman signatures [9].

2. Samples and experiments

Silica samples studied in this work are obtained from quartz fusion and have low OH and Aluminium contents. The measured glass transition temperature of this SiO_2 glass is $T_g = 1260^\circ\text{C}$. All the samples were heat treated at different annealing temperatures for 100 minutes excepted the samples heat treated at 1100°C (6 days), 1000°C (12 days), 950°C (15 days). Micro-Raman scattering experiments were performed with the 514 nm line of an Argon laser with a double XY-Dilor monochromator or with a Renishaw RM 1000 spectrometer equipped with a 514 nm notch filter. Light scattering, both elastic (Rayleigh) and inelastic (Brillouin), was obtained with a 5 gratings Z40 Dilor monochromator in a perpendicular geometry. The scattered light measurements in the different samples were all normalized to the scattering of a Suprasil glass sample.

3. Density and density fluctuations

Density of the different silica samples were determined from an Archimedes' force and are reported on the figure 1. The density increases as the fictive temperature of the samples increases between 1100°C and 1480°C. Samples heat-treated at 1000°C and 950°C have a higher density than the 1100°C sample.

‘[Insert Figure1 about here]’

A perfect homogeneous solid do not scatter light. However in a single component glass the scattering occurs through both the propagating fluctuations (Brillouin scattering) and non propagating diffusive fluctuations (Rayleigh scattering). Those density fluctuations $\langle \Delta \rho^2 \rangle$ at a given temperature T are [11]:

$$(1) \quad \langle \Delta \rho^2 \rangle = \frac{\rho^2}{V} \left\{ k T_f (\beta_T - \beta_s) + k T_f (\beta_s - (\rho v^2)^{-1}) + k T (\rho v^2)^{-1} \right\}$$

where k is the Boltzmann constant, β_T and β_s the isothermal and adiabatic compressibilities respectively and v is the sound velocity. The elastic Rayleigh scattering corresponds to the first part of the formula (1) depending on T_f which

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5 represents the density fluctuations frozen at T_f ; the second part, depending on the
6 actual temperature of the experiment T , is responsible of the inelastic Brillouin
7 scattering. At room temperature T the Rayleigh scattering of the samples with
8 different T_f is proportional to the density fluctuations frozen at T_f . Normalized to
9 the Rayleigh scattering of a Suprasil 1 glass sample, the Rayleigh scattering
10 intensity of the studied samples is shown on the figure 2 as function of the
11 annealing temperature.
12

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14 [Insert figure 2 about here]

15
16 A linear increase of the Rayleigh scattering is observed with the annealing
17 temperature from 1100°C up to 1480°C. Two samples annealed at 1000°C and
18 950°C correspond to higher scattering intensities outside the linear correlation.
19

20 Small Angle X-ray Scattering experiments on the same samples have shown
21 a similar behaviour for the density fluctuations although the scattering entities
22 analysed in SAXS experiments can have different sizes due to the difference of
23 wavelength between visible light and X-rays [10].
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26 27 4. Discussion

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29 A density increase with increasing fictive temperature between 1100°C and 1480°C
30 is observed from our results and previous measurements [5][7]; it is also correlated
31 with the increase of the sound velocity during in-situ experiments [3]. The present
32 results demonstrate further an increase of the density fluctuations with the increase
33 of the annealing temperature between 1100°C and 1480°C i.e. the silica glass
34 becomes more heterogeneous when the temperature increases. These
35 heterogeneities which are observed both with a visible light wavelength and X-rays
36 are assumed by Schroeder et al [12] to be in the nanometre range. Comparison of
37 figure 1 and 2 demonstrates that both macroscopic density and microscopic density
38 fluctuations increases with fictive temperature between 1100°C and 1480°C. It is
39 worth to notice that the relative change for density fluctuations between 1100°C
40 and 1400°C is 17% .
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43 The same correlation between density and density fluctuations is observed for the
44 samples heat-treated at 950°C and 1000°C: both increase when the temperature
45 decreases. The analysis of these samples is not straight forward as it is necessary to
46 take into account the relaxation time which, below T_g , becomes very long. For
47 example from the data of Sen [7] for pure silica, with impurities less than 1 ppm
48 and a hydroxyl concentration of 175 ppm, the relaxation time is estimated to be
49 $\tau_1 = 10$ hours at 1000°C whereas from a linear extrapolation of high temperature
50 viscosity measurements we found for the same sample $\tau_2 = 20$ days. Our samples
51 have been treated for 12 days at 1000°C and then are supposed to have relaxed if
52 we consider τ_1 value whereas it is still out of equilibrium if we take τ_2 value for
53 the relaxation time. If the first hypothesis is correct it confirms the previous results
54 [5][7] and allows to describe both microscopic density fluctuations and
55 macroscopic density curves as curves with a minimum below T_g .
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This result is important and has to be correlated with the interpretation of the anomaly of silica between its two extrema, minimum and maximum, as a soft transition region between two amorphous states of SiO_2 [7]. This is in agreement with simulation results for water where a liquid-liquid transition is observed with a density minimum [2] and with simulations of silica glass melts [13-14]. These anomalies are experimentally observed in every case[5][7] in silica glasses with low OH content which correspond to longer relaxation times at a given temperature. Furthermore our results demonstrate that in this case it is not only a macroscopic effect on density but also a microscopic effect in the density fluctuations which shows a minimum at high temperature.

Temperature dependence of the transverse and longitudinal sound velocities, deduced from in-situ Brillouin experiments [3][4] shows also an increase up to 1500 K. Longitudinal and transverse modulus C_{11} and C_{44} are calculated assuming a monotonous decrease of the density. If alternatively an evolution of the density with a minimum and a maximum is accepted the values of the elastic moduli and of the compressibility should be reanalysed although the relative variation of the density are weaker than those of the sound velocity and likely in the error bars.

5. Conclusion

Density and density fluctuations of silica show parallel behaviours. Density fluctuations, as the macroscopic density, increase from 1100°C up to 1480°C. The density minimum, previously observed, is also correlated with a minimum in density fluctuations. Further experiments are in progress to check the equilibrium of the samples heat-treated at 950°C and 1000°C.

Anomalies in density fluctuations with both a minimum and a maximum, correlated with similar macroscopic density variations predicted from molecular dynamics simulations [13-14] provide stimulating data for the study of the polyamorphism of silica.

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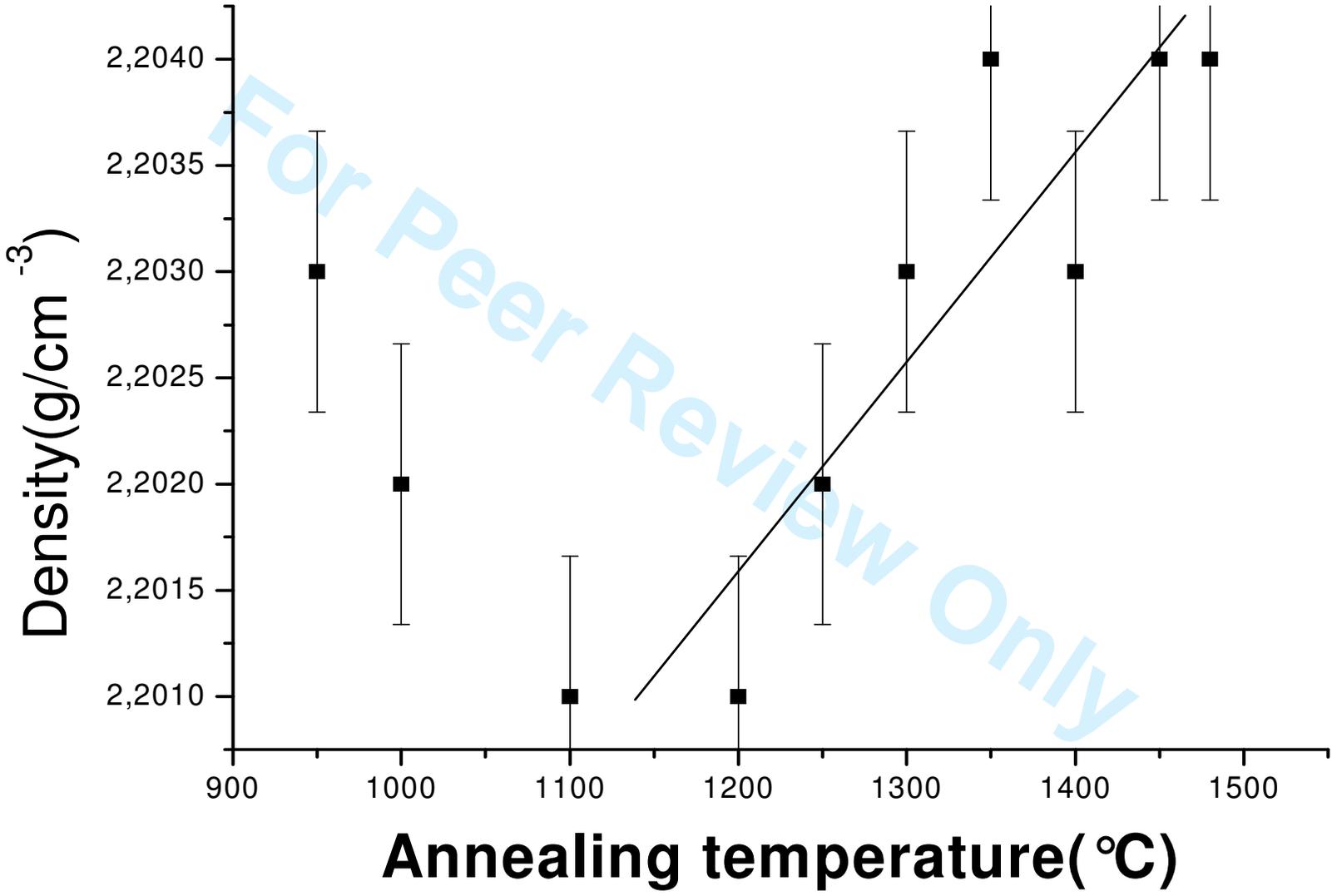
Figure captions

Figure 1

Density of the silica glass samples as function of the annealing temperature.

Figure 2

Rayleigh light scattering of the silica glass samples studied relative to a Suprasil 1 glass sample as function of the annealing temperature.



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