Pressure dependence of density and structural relaxation of glass near the glass transition region

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Abstract

A simplified and effective pressure cell together with an experimental procedure has been developed and applied to compress samples of SCHOTT N-BK7[®] glass under static high pressures in a piston-cylinder apparatus. Results from the density and volume recovery measurements show that, the glass samples were effectively densified in piston-cylinder apparatus with the density at room temperature increasing linearly with frozen-in pressure. To explain the experimental data, we developed a mathematical model based on a suggestion by Gupta (1988) with two internal parameters, named fictive temperature (T_f) and fictive pressure (P_f), which fits the experimental data well.

Key words: Glass; High pressure; Piston-cylinder apparatus; Structural relaxation; Fictive temperature; Fictive pressure.

1. Introduction

It is well known that the properties of glass at room temperature are influenced by temperature, particularly around the glass transition region¹. Glass is not in equilibrium, but instead, the structure and properties of glass are time-dependent while it aims to reach equilibrium^{2,3}. The temperature and time-dependence of properties as well as the structural relaxation of glass in the glass transition region have been well-characterized experimentally and can be explained with several mathematical models^{1, 2, 4, 5, 6}. Yet, those studies were all performed for 1 bar, and did not consider the effect of increases in pressure.

However, pressure also changes the properties and the behavior of glass even at room temperature. Experimental examples are hardness measurement^{7,8} and scribing of glass. In the glass transition range, the viscosity strongly depends on density⁹ and thus on pressure. For example, Bridgman and Simon¹⁰ compressed thin samples of oxide glasses (SiO_2 and B_2O_3) and several mixed silicate glasses samples between two flat dies (uniaxial) made of carboloy at room temperature, and demonstrated that the vitreous SiO_2 had a density increase of almost 7.5% at 20 GPa, whereas the vitreous B_2O_3 has an asymptotic increase of density near 6% at pressures close to 20 GPa. An experimental study on a borosilicate glass with pressure of up to 0.66 GPa and temperatures up to 300°C, showed that the density change was very small with only 0.05% at 0.66 GPa, 200°C and 24 hours¹¹. A compilation of experimental data shows that there are significant differences in the manner in which different glass-types react

to increases in pressure¹². Jin et al.¹³ reported a 6 K/GPa change in T_g of a metallic glass by DSC measurements, and activation volume was suggested to describe the pressure dependence of glass relaxation in a free volume model.

Several phenomenological models^{14, 15, 16, 17} describe the time dependent frozen-in state and departure from equilibrium (δ)¹⁹ of glass forming materials depending on temperature history^{4, 5, 18} and also pressure history^{14, 15, 16, 17}. Those models are based on the Tool-Narayanaswamy-Moynihan^{4, 5, 18} model and use one internal parameter named fictive temperature (T_f). On the other hand, Davies and Jones²⁰ pointed out that fictive pressure (P_f) could also be an internal parameter. Gupta²¹ introduced the P_f to his structural relaxation model as an internal parameter together with T_f , but has not compared his two-internal-parameter model to experimental data.

Here, we present new experimental data to study the density and structural relaxation of glass under elevated pressure of up to 1.5 GPa and elevated temperature, which were obtained using a piston-cylinder apparatus. We describe the new experimental procedure developed for this as well as a two-internal-parameter model that can overall fit the data.

2. Experimental procedure

2.1 Samples

The SCHOTT N-BK7[®] glass samples had been originally cooled at a rate of -0.4 K/h at ambient pressure and machined to cylinders with diameters of 7.40 ± 0.02 mm and

heights of 6.00 ± 0.02 mm for the experiments. The density of those slow-cooled samples at room temperature is 2.5082 ± 0.0006 g/cm³. The glass transition temperature $T_g = 561$ °C is taken as the temperature at which the viscosity is 10^{12} Pa·s. Specially, the sample relatively fast-cooled at a rate of -120 K/h at ambient pressure in the lab was used for comparison to the samples after high pressure treatment, as all the samples in high pressure treatment were cooled at a rate of -120 K/h. The density of this fast-cooled sample at room temperature is 2.4957 ± 0.0007 g/cm³.

2.2 High pressure treatment

Test equipment: A self-assembled piston-cylinder apparatus²² with an improved design based on the principle of Boyd and England²³ with uniaxial pressure up to 3 GPa was applied for the high pressure treatment. The uncertainty of pressure in the piston-cylinder apparatus was ± 0.05 GPa.

Pressure cell development: A special pressure cell needed to be developed, to obtain glass samples with no cracks at the end of the experiments such that we obtain sufficient material for further measurements. If not, during subsequent measurements, the cracks in the sample may open and increase the apparent macroscopic volume of the sample, which erroneously would be interpreted as a decrease in density.

Experimental process: The experimental processes of high pressure treatment are shown in Fig.1 (a). Glass samples are first subjected to high pressures and then heated up to 700 °C at 600 K/h. The temperature is chosen for the glass to be viscous enough for a hydrostatic pressure state to build up and to avoid crystallization. After keeping the

temperature fixed for 24 hours (2 hours for the 1 GPa sample at the first experiment), the samples are relatively fast-cooled at -120 K/h to room temperature. Pressure release is done at a rate of -0.2 GPa/h to 0.5 GPa and further at a lower rate of -0.05 GPa/h to 0.1 MPa (-1.5 GPa/h to 0.1 MPa for 1.25 GPa sample due to the programming error, purple line with open stars in Fig.1 (a)). Glass samples reach stage ① after this process.

Fig. 1 (a) Process of high pressure treatment in piston-cylinder apparatus; (b) process of volume recovery measurements in dilatometer for all the samples. Arrow in (a) shows the time sequence of high pressure treatment. Stage ①: samples compressed by high pressure and before volume recovery measurement; Stage ②: samples reach

equilibrium in dilatometer at 525 °C; Stage ③: samples cooled down from 525 °C and moved out from the dilatometer.

Stress condition: The stress state in the glass sample in the piston-cylinder apparatus is influenced by gaps in the pressure cell that develop during assembling, especially the gap from sample to the other parts, the stiffness and Poisson's ratio of the insulator¹² and by the thermal expansion coefficients of the materials used for the pressure cell. To make the glass sample more deformable than the surrounding materials, it is heated up to a temperature of 700 °C at which it behaves mainly viscous such that the glass sample obtains a hydrostatic stress state. During cooling, the glass changes from mainly viscous to frozen-in, during which the hydrostatic stress state may change into a uniaxial stress state. Therefore, the frozen-in stress state is not known precisely. For the calculations, we assume a hydrostatic stress state always. Compared to this uncertainty in the overall stress state, the stress introduced to the sample by the frozen-in temperature gradient during cooling is small.

2.3 Density measurement

Test equipment: The Mettler Toledo-XP205 was used for the density measurement using the Archimedes principle. The density uncertainty was calculated by the statistical uncertainty from the 95% confidence interval of the student's t-test and the standard deviation.

Experimental process: Firstly, the mass of the samples was measured in air, then the mass of samples in the liquid was measured and the temperature of the liquid was recorded at the same time. Each sample was measured 5 times and the results reported

are the average values rounded to four decimals.

2.4 Volume recovery measurement

Test equipment: The Bähr DIL 806 optical dilatometer is used to measure the length change of the sample diameter without mechanical contact. The temperature of the dilatometer has been calibrated by a pure quartz crystal with a repeatability of α - β transformation temperature of ± 0.39 °C in the same position.

Experimental process: The change in diameter was measured by applying the temperature history shown in Fig.1 (b). The dilatometer was heated from room temperature to 500 °C at a rate of +1200 K/h, then at +120 K/h to 525 °C and holding for 72 hours. At the end of this isothermal hold the sample diameter does not change any more. This equilibrium state is denoted as stage ②. Afterwards, the samples were freely cooling down to the room temperature, at which they reached stage ③.

3. Results

3.1 High pressure treatment

The standard pressure cell (1#) for rock experiment resulted in a glass sample broken to many pieces. Thus, we designed and prepared the other four pressure cells seeking for a suitable pressure cell for the high pressure experiments to obtain glass samples with no crack and no blackening. The designed pressure cells and accordingly images of glass samples after high pressure treatment are shown in Fig.2.

Fig. 2 Pressure cells development and images of glass samples after high pressure treatment for different pressure cells. 1-Pyrophyllite; 2-Steel plug; 3-Thermocouple; 4-Graphite; 5-NaCl; 6-Sample; 7-Pt; 8-Al₂O₃; 9-Borosilicate glass; 10-h-BN.

Pressure cell 1#: The sample was in a welded Pt capsule. The inner insulator of alumina ceramic acts as the pressure transmitting medium. The borosilicate glass separates it from the pure NaCl powder which acts as the outer insulator. The 1 GPa treatment resulted in a glass sample that was broken into many pieces, which indicates that this pressure cell is not suitable for very high pressures.

Pressure cell 2#: The borosilicate glass was removed, because it is not ductile at low temperature and it broke with a load noise during the pressurization which made the

pressure cell less isostatic. The NaCl was used as the outermost sleeve and low spacer for the Pt capsule because it behaves like a liquid even at low temperature, and thereby transmits more isostatic pressure to the furnace and the sample. The 0.5 GPa treatment resulted in a sample with only few cracks on the surface.

Pressure cell 3#: Compared to 2#, the Al_2O_3 ceramic and Pt capsule were replaced by insulating hexagonal boron nitride (h-BN). The h-BN has a graphite structure, which makes it behaves like a lubricant and leading to a more isostatic compression. The 1.5 GPa treatment resulted in a sample with a thin black layer outside and large amounts of cracks inside.

Pressure cell 4#: Based on 3#, the h-BN was kept, and a Pt sleeve was added to separate the sample from the h-BN sleeve. The 0.9 GPa treatment resulted in an optically black sample with an approximately 0.4 mm thick crystal layer outside. This crystal layer was ground off before further measurements to obtain a sample with cylindrical shape without any cracks.

Pressure cell 5#: To avoid blackening of the sample, a sealed Pt capsule replaced the Pt sleeve. However, the 1.25 GPa treatment resulted in a sample with considerable blackening and lots of fractures inside, which indicates that sealing with Pt cannot solve the blackening problem.

For further measurements, we used the pressure cell 2#, because 2# was the only pressure cell which obtained glass sample without cracks and blackening. The further compression treatment at 0.75 GPa and 1.1 GPa resulted in only small amounts of

cracks at the surface and no blackening inside (similar to the 0.5 GPa sample). Moreover, the slight black film on the 1.1 GPa sample disappeared during the volume recovery measurement. Therefore, the pressure cell 2# is suitable for compressing glass.

3.2 Density after high pressure treatment

In the high pressure treatment, the glass samples were cooled at the fast cooling rate of -120 K/h to room temperature (Fig.3, stage ①). Compared to the fast-cooled uncompressed sample with density of $2.4957 \pm 0.0007 \text{ g/cm}^3$, their density increases approximately linearly with pressure, which can be fitted with:

$$\rho = 0.0723P + 2.4958 \quad (1)$$

where ρ is the density of the sample at room temperature in g/cm^3 , P is the applied pressure in GPa. Specifically, the density increased by 4.49% after the 1.5 GPa treatment. The sample compressed at 1 GPa (red square in Fig.3) broke into several parts which led to a very high uncertainty.

Fig. 3 Density of glass samples at three different stages: Stage ① = at room temperature after high pressure treatment; Stage ② = at 525 °C, at the end of the

volume recovery measurement (= equilibrium density); Stage ③ = at room temperature after free cooling from Stage ②.

Moreover, from the density in stage ① and the measured relative length change (Fig.4) during heating up and isothermal hold (Fig.1 (b)) for volume recovery, the time dependent specific volume at 525 °C was calculated. At the end of the isothermal hold (stage ②), all the samples reached similar equilibrium densities of around $2.4602 \pm 0.0011 \text{ g/cm}^3$ at 525 °C. After free cooling to room temperature (stage ③), the density of all samples increased to approximately $2.4958 \pm 0.0056 \text{ g/cm}^3$, with most measurements having a higher uncertainty than before.

The 1 GPa and 1.25 GPa samples that were treated with different experimental procedures are not used for further volume recovery measurements.

Fig. 4 Relative length change of samples versus time at volume recovery temperature of 525 °C.

3.3 Volume recovery

The measured relative length changes in diameter during volume recovery of the uncompressed samples were smaller in magnitude than those of the compressed samples (Fig.4), which go from an increase in diameter of 1.03 % after 0.5 GPa compression to 1.89 % after 1.5 GPa compression. Particularly, the two arrows in Fig.4 indicate that the 1.1 GPa curve shows fluctuations after reaching equilibrium and lost data points after approximately 37 h (the sample was broken up which caused measurement error). The difference between these two arrows in relative length change is only approximately 0.02%, which leads to an uncertainty in specific volume of $\pm 0.0003 \text{ cm}^3/\text{g}$. This sample does not reach 72 h, therefore does not contribute to the average specific volume. During the volume recovery, the more the samples have been compressed in the high pressure treatment, the more the measured change in relative length increases.

3.4 Mathematical Model

To describe the measured volume recovery, we firstly applied the exponential decay model^{3, 19, 24, 25}, which fits the data well but reached different relaxation times in the new equilibrium state at 525 °C and 1 bar. A new mathematical model is developed following the suggestion by Gupta²¹, in which the volume relaxation depends on two internal parameters, named fictive temperature $(T_f)^4$ and fictive pressure $(P_f)^{21}$, to account for the thermal history and the pressure history.

The mathematical model assumes a true hydrostatic stress during the whole high

pressure treatment. The specific volume depends on T, T_f, P, P_f according to

$$V = V_{ref} \exp [J_{froz}(P_{ref} - P) + \Delta J(P_{ref} - P_f) + 3\alpha_{froz}(T - T_{ref}) + 3\Delta\alpha(T_f - T_{ref})] \quad (2)$$

with $T_{ref} = 525$ °C, $P_{ref} = 0.0001$ GPa, and $V_{ref} = 0.4065$ cm³/g. The rates of change in fictive temperature T_f and fictive pressure P_f

$$-\frac{dT_f}{dt} = (L_{TT}\frac{\Delta C}{T} - L_{TP}V\Delta\alpha)(T_f - T) + (-L_{TT}V\Delta\alpha + L_{TP}V\Delta J)(P_f - P) \quad (3)$$

$$-\frac{dP_f}{dt} = (L_{TP}\frac{\Delta C}{T} - L_{PP}V\Delta\alpha)(T_f - T) + (-L_{PT}V\Delta\alpha + L_{PP}V\Delta J)(P_f - P) \quad (4)$$

are taken from Gupta²¹. Here, $\Delta C = C_{liq} - C_{froz}$ is the specific heat capacity of the liquid (equilibrium) state C_{liq} and the frozen (glassy) state C_{froz} . Similarly, $\Delta\alpha = \alpha_{liq} - \alpha_{froz}$ is the difference in thermal expansion coefficient between liquid and frozen glass, $\Delta J = J_{liq} - J_{froz}$ is the difference in compressibility between liquid glass and frozen glass with $J = 1/K$ (K is the bulk modulus). L_{TT} , L_{TP} , L_{PT} and L_{PP} are kinetic coefficients²¹ which depend on T, P, T_f and P_f . For the model in this report, the assumptions $L_{TT} = \frac{T}{\Delta C\tau_c}$, $L_{TP} = L_{PT} = \frac{1}{V\Delta\alpha\tau_\alpha}$ and $L_{PP} = \frac{1}{V\Delta J\tau_J}$ are used. This introduces three time constants: τ_c for changes in specific heat, τ_J for changes in compressibility, and τ_α for changes in thermal expansion coefficient. Those three different time constants

$$\tau_c = f_c\tau_G \quad (5)$$

$$\tau_\alpha = f_\alpha\tau_G \quad (6)$$

$$\tau_J = f_J\tau_G \quad (7)$$

differ from the characteristic time τ_G for changes in the shear modulus by constant factors f_c , f_α , f_J only.

Following the idea of Markovsky and Soules²⁶, the T_{f_new} and P_{f_new} at the end of a time step Δt are calculated from the T_{f_old} and P_{f_old} at the beginning of the same time step Δt .

$$T_{f_new} = \frac{T_{f_old}\tau_\alpha\tau_c + (\tau_\alpha - \tau_c)T\Delta t + (-TV\Delta\alpha\tau_\alpha/\Delta C + \Delta J\tau_\alpha/\Delta\alpha)(P - P_{f_old})\Delta t}{\tau_\alpha\tau_c + (\tau_\alpha - \tau_c)\Delta t} \quad (8)$$

$$P_{f_new} = \frac{P_{f_old}\tau_\alpha\tau_J + (\tau_\alpha - \tau_J)P\Delta t + (\Delta C\Delta J/(V\Delta\alpha T) - \Delta\alpha\tau_\alpha/\Delta J)(T - T_{f_old})\Delta t}{\tau_\alpha\tau_J + (\tau_\alpha - \tau_J)\Delta t} \quad (9)$$

In the model of this report, the characteristic time constant for changes of the shear modulus

$$\tau_G = \tau_{ref} \exp \left\{ \frac{x}{T} \left[\frac{\Delta H}{R} + f_p \frac{\Delta V_a}{R} (P - P_{ref}) \right] + \frac{1-x}{T_f} \left[\frac{\Delta H}{R} + f_p \frac{\Delta V_a}{R} (P_f - P_{ref}) \right] - \frac{\Delta H}{RT_{ref}} \right\} \quad (10)$$

depends on real pressure and fictive pressure via an apparent activation volume^{13, 27} ΔV_a ($\Delta V_a = M_{mol}V_{ref}$) with a percentage factor of f_p ($0 \leq f_p \leq 1$) and $\tau_{ref} = 0.45 h$. In case of $P_f = P = P_{ref}$, the characteristic time $\tau_G(T, T_f, P, P_f)$ reduces to the characteristic time τ in the Tool-Narayanaswamy^{4, 5} model

$$\frac{dT_f}{dt} = \frac{T - T_f}{\tau} \quad (11)$$

$$\tau = \tau_{ref} \exp \left[\frac{x\Delta H}{RT} + \frac{(1-x)\Delta H}{RT_f} - \frac{\Delta H}{RT_{ref}} \right] \quad (12)$$

where T_f is the fictive temperature and x is a fixed factor.

This mathematical model captures the influence of the pressure pre-history on the volume recovery measurements at 525 °C with a single set of parameters (see figure caption for employed constants in Fig.5 (a)). The calculation for each sample comprises the initial cooling at fast or slow cooling rate, the high pressure treatment (if any), the heating-up stage and, finally, the isothermal volume recovery measurement.

Fig. 5 (a) Measured volume recovery data fitted by the new model with $\Delta H/R=74000$ K, $x=0.6$, $f_c=2$, $f_J=3$, $f_\alpha=20$, $K_{liq}=20$ GPa, $f_p=1$. (b) Change of T_f and P_f of fast-cooled samples versus time in our mathematic model.

The calculated temporal change of T_f and P_f is given in Fig.5 (b). P_f starts close to the real pressure of the compression treatment at the beginning of the isothermal stage, and then gradually decreases to ambient pressures. Particularly, the model gives a negative value (close to 0) of P_f for the uncompressed fast-cooled sample until approximately 10 hours. On the other hand, T_f is also strongly influenced by fictive pressure and goes down to lower than 525 °C before gradually back to 525 °C. This is similar to the crossover phenomenon which has been reported in studies^{1,28} on refractive index of glass. In our model, the T_f and P_f are coupled. The coupling is at different time constants which leads to the crossover during approaching to the equilibrium value. The compression treatment increases the calculated T_f at the beginning of the volume recovery as a function of

$$T_{f_begin} = 7.04P_{f_begin} + T_{f_begin_0} \quad (13)$$

where $T_{f_begin_0} = 533.15$ °C is the fictive temperature of the uncompressed fast-cooled sample when it firstly reaches the volume recovery temperature of 525 °C. At the zero time in Fig.5, the glass sample is still frozen-in. The glass sample is gradually wake-up and reaches the volume recovery temperature at approximately 0.6 hour. After a recovery time long enough, all samples reach the same calculated $T_f = 525$ °C, $P_f = 0.0001$ GPa.

At the beginning of the isothermal volume recovery, the time constant τ_{G_begin} increases approximately linear with fictive pressure (Fig.6)

$$\tau_{G_begin} = 3.50P_{f_begin} + \tau_{G_begin_0} \quad (14)$$

where $\tau_{G_begin_0} = 0.30 \text{ h}$ is the characteristic time when the uncompressed fast-cooled sample first reaches 525 °C. Based on the Maxwell relationship²⁹ on shear modulus relaxation time

$$\tau_G = \eta_s / G_\infty \quad (15)$$

where η_s is the shear viscosity and G_∞ is the unrelaxed shear modulus (34 GPa of SCHOTT N-BK7[®] glass), the viscosity of glass increases with pressure as does the characteristic time τ_G .

Fig. 6 τ_G and T_f of fast-cooled samples at the beginning of the isothermal volume recovery at 525 °C as a function of fictive pressure in our mathematic model.

4. Discussion

In our experiments, sample blackening occurred during pressurization of silicate glasses in all pressure cells using h-BN as pressure transmitting medium. The mechanism of blackening is not clear. Brooker et al.³⁰ reported that it may be caused by carbon infiltration³⁰ from the graphite furnace. The blackening of 0.9 GPa sample was not reversible at 525 °C and showed no absorption bands measured in the transmission spectrum. On the other hand, the sample from the 1.1 GPa experiment (no h-BN) became visibly clear after heating up again in air to 525 °C during the volume recovery, which may thus be due to the reduction of oxygen³¹ in the glass and different from the nonreversible blackening.

We note that the shapes of length change curves in Fig.4 are not exactly the same although the overall change is quite regular. This is attributed to the measurement accuracy of the optical dilatometer. The volume recovery shows that, at sufficiently high temperature and holding time, the densification of glass under high pressure is reversible¹¹. The isothermal hold of 72 h at 525 °C is sufficient for SCHOTT N-BK7[®] to reach the equilibrium state in our experiments. During the 72 h isothermal hold, the cracks in the sample might have changed (especially cracks might have opened), therefore, at stage ③, the uncertainty of density could become larger.

The solution for the mathematical model used in this work is not unique. The bulk modulus of the solid glass is $K_{froz}=46.5$ GPa, from which one can estimate $K_{liq}=K_{froz}/3=15.5$ GPa following a rule of thumb. The change of density with applied pressure (Fig.3) gives a bulk modulus of approximately $K_{liq}=20.1$ GPa. Our

mathematical model (Fig.5 (a)) uses $K_{liq}=20\pm2$ GPa to describe the experimental data. The K_{liq} has a strong influence on the specific volume at the beginning of the isothermal volume recovery in this model. To improve the model, one could also introduce weight factors to discriminate silicate from the other compositions like Narayanaswamy⁵, at the cost of requiring more free parameters.

The new model developed in this work can also be used to predict the volume recovery of SCHOTT N-BK7[®] under various pressure and temperature histories. For example, in Fig.7, we model the volume recovery experiments at a heating rate of 600 K/h to 700 °C for 4 samples with different temperature and pressure histories, fast-cooled (-120 K/h) at 1 bar, slow-cooled (-0.4 K/h) at 1 bar, fast-cooled at 1 GPa, and slow-cooled at 1 GPa, respectively. The peak temperature (T_{peak}) is taken from the peak value of the $\alpha_v = \frac{1}{V} \frac{dV}{dT}$ in Fig.7 (a). The T_{peak} of samples (values are shown in Fig.7 (a)) after 1 GPa high pressure treatment (with higher P_f at the beginning) are increased only by approximately 5 °C. The α_v starts to change early at around 540 °C and finish rather abruptly at around 600 °C. The high overshoot of the slow-cooled samples at -0.4 K/h is due to the 3 orders magnitude difference in cooling rate.

Fig. 7 (a) Prediction of the volume recovery at a constant heating rate after various temperature and pressure treatments from our mathematic model. (b) Corresponding change of T_f and P_f in our mathematic model.

5. Conclusions

The effects of high pressure on density and volume recovery of SCHOTT N-BK7[®] glass near the glass transition region has been measured and quantitatively described in this work.

- (1) A simplified and effective pressure cell (2#) together with an experimental process is developed to compress glass at high pressures around the transition region using a piston-cylinder apparatus.
- (2) Glass samples can be effectively densified in the piston cylinder apparatus with an approximately linear increase in density at increasing pressure.
- (3) A mathematical model with two internal parameters is developed that describes the volume recovery of all samples with a single set of parameters.

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