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Structural relaxation mechanisms in hydrous sodium borosilicate glasses

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ABSTRACT

Borosilicate glasses ($16Na_2O–10B_2O_3–74SiO_2$, NBS) with water contents up to 22 mol% H_2O were prepared to study the effect of water on structural relaxation using DTA, viscometry and internal friction measurements. The results show that the glass transition temperature T_g of DTA and *the* isokom temperature T_{12}, of viscometry are in excellent agreement, confirming the equivalence of enthalpy and viscous relaxation for NBS glass. Combining T_g data with water speciation data demonstrates that OH groups are mainly responsible for the decrease of T_g with increasing hydration, while molecular water plays only a minor role. Internal friction spectra at 7.125 Hz confirm the decisive influence of water on mechanical relaxation. The temperature range of α-relaxation (glass transition) strongly decreases while two β-relaxation peaks (sub-T_g) progressively appear with increasing water content. A high temperature β-relaxation peak, attributed to the presence of OH groups, shifts from 670 to 450 K as total water content increases from 0.01 to 5 wt%. A low temperature β-relaxation peak, attributed to molecular water, appears at 380 K and 330 K in glasses containing 3 and 5 wt% H_2O, respectively. These findings suggest that relaxation mechanism of different hydrous species at low temperature may contribute to fatigue of stressed glasses.

1. Introduction

It is well known that water plays an important role in the structure and properties of silicate melts and glasses. This is particularly the case for natural glasses, in which several weight percent of water can be dissolved due to elevated pressures [1,2]. The investigation of water in industrial relevant glasses is also a crucial issue, since water has drastic influence on mechanical relaxation phenomena. Viscosity can be strongly reduced upon hydration [3], e.g., ≈3 wt% water decreases the glass transition temperature T_g by > 30% for numerous glasses. Stress relaxation is also enhanced, a phenomenon used for instance to strengthen glass fibers by exposing them to water vapor under stress [4,5]. Furthermore, low temperature processes in glasses such as internal friction [6,7], aging [8], crack growth and fatigue [9,10,11] may be affected even by small amounts of water. For instance, ambient moisture can enhance sub-critical growth rate in soda-lime-silicate glass by up to 4 orders of magnitude [12]. Such sub-T_g processes can be of relevance also in nature, e.g. in the fragmentation of ascending magmas during volcanic eruptions.

Wiederhorn [12] showed that sub-critical crack growth (SCCG) is strongly affected by the mechanical properties of the crack tip near the cohesive region. Water can be easily adsorbed at the crack tip, leading to stress corrosion [13], reduction in surface energy [14], and bond strength [15]. However, crack propagation can also be affected by entry of water into the glass structure at the crack tip [9], accelerated by tensile stress at the crack tip [16]. As a consequence, mechanical relaxation and elastic moduli change locally very strongly [17]. Since these local phenomena are difficult to measure in situ, we used studies on hydrous glasses to mimic such relaxation phenomena.

Network relaxation in the range of the glass transition is well investigated for a wide range of hydrous and anhydrous silicate and aluminosilicate glasses [2,18,19]. Considerable less information is available about relaxation processes in hydrous boron-bearing glasses. It is known that water in glasses is present as two main species in glasses: as molecular water (H_2O_{mol}) and as dissociated water forming OH groups [20–23]. In silicate and aluminosilicate glasses the strongest decrease of the glass transition temperature T_g upon incorporation of water occurs in the range of low water contents (≤2 wt% H_2O), where OH groups are the predominant water species. At water contents above ~3 wt% the content of hydroxyl groups apparently level off, and the amount of molecular water rises strongly. This trend is a consequence of the decrease in fictive temperature of the glass with increasing water

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content, i.e. water speciation is frozen in at lower temperatures.

Only a few studies on the speciation of water in borosilicate and boroaluminosilicate glasses with high water contents (up to 10 wt% H_2O) are available [20,21,24,25]. These studies revealed that OH groups are increasingly stabilized with increasing boron content. While molecular water is the dominant water species at water contents > 7 wt% H_2O in borosilicate and boroaluminosilicate glasses, only ~1 wt% molecular H_2O was found in soda-lime borate glasses with 7.5 wt% H_2O [22].

In the three-component model of Tomozawa [23] the influence of water species and dry glass component was considered to model the decrease of the glass transition temperature with increasing water content. Deubener et al. [3] applied this concept to a variety of silicate and aluminosilicate glasses and showed that the effect of OH groups on T_g is by far stronger compared to that of molecular water in these compositions. The limitation of this concept so far has been that the applied water speciation data measured on the glasses do not represent T_g since the cooling rate of the glasses differs from the standard cooling rate [26].

There is only rare knowledge about the influence of total water and water species on sub-T_g relaxation in oxide glasses [27]. Internal friction measurements indicate up to three relaxation modes in glasses. These modes are often denoted as α-, β-, and γ-relaxation in the order of decreasing temperature [28–30]. The dominating α-relaxation mode is mainly responsible for viscous flow, stress relaxation and internal friction at elevated temperatures [28]. Typically, only the low-temperature flank of this broad peak can be measured, and the maximum is supposed to be close to T_g. With increasing water content, the α-relaxation peak and T_g shift to lower temperatures [28,31].

In some glasses an additional relaxation mechanism, labeled as β-relaxation, has been observed as a shoulder on the low temperature flank of the α-relaxation peak and has been assigned to movements of non-bridging oxygens (NBOs) [7,30], cooperative movements of equal or dissimilar mobile species such as alkali or alkaline-earth ions [28,32–37] or movements within a cluster of alkaline-earth cations [30]. In water-poor (≤ 0.3 wt% H_2O) phosphate, borate and silicate glasses β-relaxation was correlated with cooperative motions of alkali ions and neighboring protons [38–42]. β-relaxation phenomena in glasses with high water contents, when a significant amount of molecular water is present, are rarely investigated. In the study of Reinsch et al. [27] two distinct β-relaxation peaks in mechanical loss spectra were attributed to dynamics of OH groups and molecular water in hydrated silicate glasses (≤ 1.9 wt% H_2O). The relaxation mode of H_2O_{mol} was found to be faster compared to OH groups and is probably caused by jumps of H_2O molecules between adjacent cavities in the network. It is worth noting that rotation of H_2O molecules around their bisector axis, another low temperature process in hydrous glasses identified by NMR spectroscopy and quasielastic neutron scattering, is too fast to contribute to the β-relaxation peak [43,44]. In contrast to α-relaxation, which governs global network relaxation, β-relaxation may be considered as a more regional process embedded within the much more rigid global network.

The γ-relaxation mode, observed at temperatures < 373 K [45], is attributed to the motion of alkalis, since the range of activation energies ($E_\gamma \approx 63$–$105\ \mathrm{kJ\ mol^{-1}}$) [46] resembles those of alkali diffusion (63–$84\ \mathrm{kJ\ mol^{-1}}$) [7]. In contrast to α- and β-relaxation, γ-relaxation is more a local phenomenon.

Our study is aimed to improve the understanding of the influence of water content and speciation on mechanical relaxation in borosilicate glasses using differential thermal analysis (DTA), sphere penetration viscometry (SPV), and dynamic mechanical analysis (DMA) to study relaxation mechanisms. The composition of the investigated borosilicate glass (16 mol% Na_2O, 10 mol% B_2O_3 and 74 mol% SiO_2) was chosen as representative for a technical glass since the borosilicate crown glass BK7 from Schott AG is very similar in composition. A detailed characterization of the anhydrous and hydrous borosilicate glass structure was published in Bauer et al. [24], including analysis of water speciation, boron speciation as well as Q^n-speciation (SiO_4 tetrahedron with n = number of bridging oxygen).

2. Experimental and analytical methods

2.1. Sample preparation

For the synthesis of the borosilicate glass a powder mixture of Na_2CO_3, B_2O_3 and SiO_2 was used. A detailed description of the synthesis is given in Bauer el al. [24]. Samples with 0.2 wt% H_2O were synthesized from the base glass in 110 ml alumina crucibles by re-melting and water steam bubbling at 1753 K and 0.5 MPa argon pressure within 3 h. Subsequently, the temperature was lowered, and the melt was cooled with $3\ \mathrm{K\ min^{-1}}$ through the regime of ($T_g \pm 150$ K) to avoid internal stress in the glasses. The procedure was described in the study of Reinsch et al. [27]. Electron probe microanalysis indicate ca. 4 wt% Al_2O_3 in this particular glass. Consistency of experimental data with the other (Al-free) glasses implies that this contamination has minor effect on our study. All samples with water contents ≥ 0.5 wt% were synthesized in an internally heated pressure vessel (IHPV) at 500 MPa and 1423 K for 14–20 h using the same procedure as given in [24]. Cooling rate in the regime of glass transition was ~8 K/s for NBS0-500 MPa, NBS0.5 and NBS1, ~6 K/s for NBS3 and ~3.5 K/s for NBS5. The water-rich glass NBS8 was quenched much faster (~200 K/s) to avoid crystallization during cooling.

2.2. Differential thermal analysis

The glass transition temperature, T_g, was determined by differential thermal analysis in air using 15–20 mg of glass pieces or powdered glass placed in Pt-crucibles (thermobalance TAG 24, Setaram, Caluire, France). The same measurement routine and data evaluation (tangent method) was applied to hydrous borate glasses, and T_g values were found to be in perfect agreement with isokom temperatures (T_{12}) at which the viscosity equals 10^{12} Pa·s [22]. For each sample four heating and cooling cycles with $10\ \mathrm{K\ min^{-1}}$ were applied. The maximum temperature did not exceed T_g by > 50 K. The first cycle represents the fictive temperature T_f of the glasses, since the cooling history of the samples reflects the status of quenching after IHPV synthesis. The following three cycles were used for the determination of T_g. Definition of T_f and T_g is based on the onset of the endothermic step in the DTA curve according to Mazurin [47,48]. The average T_g values for all investigated glasses are included in Table 1.

In order to detect a possible loss of water of high water-bearing glasses, the thermal gravimetric (TG) signal was simultaneously recorded during DTA measurement. Additionally, a mass spectrometer (MS, Balzers Quadstar 421) was used for analysis of evolved gases, coupled to the DTA by a heated (453 K) quartz glass capillary. Neither a significant mass loss nor a distinct signal for water by mass spectroscopy could be detected. The good reproducibility of T_g determination further supports a negligible water loss during the DTA procedure. The maximum error of temperature for this method is ± 5 K.

2.3. Sphere penetration viscometry (SPV)

Viscosity data were obtained by sphere penetration measurements. Cylindrical samples with diameters of ~6 mm and heights of 1–2 mm were sliced from the synthesized glasses. Coplanar surfaces were obtained by grinding and polishing the sample surfaces.

The vertical dilatometer (VIS 404, Bähr GmbH) is equipped with a pushing rod made of silica glass and a sapphire sphere (radius $r = 0.75$ mm). The force applied on the pushing rod was adjusted to 3.9 N. The temperature was controlled with an S-type thermocouple (Pt-PtRh) placed in the vicinity (2–3 mm) of the sample surface. The thermal gradient along the sample axis was less than $\pm 1\ \mathrm{K\ mm^{-1}}$.

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