



Water- and boron speciation in hydrous soda–lime–borate glasses



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ABSTRACT

The structural investigation of hydrated borate glasses provides new insights on the influence of water on boron speciation using spectroscopic methods. In the present study three soda–lime–borate glasses (NCB_x with $x = 5, 15$ and 25 corresponding to $x\text{Na}_2\text{O}, 10\text{CaO}, 90 - x\text{B}_2\text{O}_3$ in mol%) were prepared with water content up to 8 wt.%. The water speciation in the glasses was derived by near-infrared (NIR) spectroscopy while boron speciation was investigated by ¹¹B MAS NMR (Magic Angle Spinning Nuclear Magnetic Resonance). For the three glasses effective molar absorption coefficients were determined experimentally for the bands at 5200 cm⁻¹ and 4600 cm⁻¹, corresponding to combination modes of H₂O molecules and OH-groups, respectively. In contrast to silicate glasses, in which at most ~2 wt.% H₂O are dissociated to OH-groups, the amount of dissociated H₂O may even exceed 5 wt.% in borate glasses. The fraction of tetrahedral to total boron ($N_4 = \text{B}^{\text{IV}} / \text{B}^{\text{IV}} + \text{B}^{\text{III}}$) is predominantly controlled by the ratio of Na₂O + CaO / B₂O₃, but only weakly affected by the water content of the glasses. When increasing the H₂O content from 0 to 8 wt.%, N_4 increases from 25% to 26% for NCB5 and from 42% to 47% for NCB25 glasses.

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1. Introduction

Boron-bearing oxide glasses were intensively investigated in the past because of their various technical applications. Alkali borosilicates have been used as thermal shock-resistant glasses, whereas alkaline earth borosilicate glasses can be applied as substrate glasses for liquid crystal displays. Technical application of pure borate glasses is very limited due to their poor chemical durability. Nevertheless, studies on such glasses can give important insight to the structural behavior of boron in oxide glasses, which is important for the development of new materials.

One special feature of such glasses is the so-called boron anomaly, which describes the property of boron to change its coordination number (CN) from 3 to 4 and back to 3 surrounding oxygens in response to the addition of network modifiers as alkalis or alkaline-earth oxides. This trend reflects the preservation of a completely interconnected framework at low contents of network modifiers, and the formation of non-bridging oxygens (NBO) which can be expressed by the equilibrium reaction (1) at high contents of network modifiers [1,2].



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In binary borate glasses ($x\text{M}_2\text{O} \cdot 1 - x(\text{B}_2\text{O}_3)$) it was observed that the increase of the fraction of tetrahedral coordinated boron occurs up to $x = 0.33\text{--}0.43$ [3–5], depending on the type of cation [4,5]. It was found that lithium is more efficient in charge compensating the B^{IV}-units than other alkalis, due to its small size [4,5].

Temperature and pressure were also found to be crucial parameters affecting the boron coordination number [6–9]. With increasing temperature the reaction in Eq. (1) shifts to the right. The decrease in boron coordination number with higher fictive temperatures (T_f) due to faster cooling is more pronounced for glasses containing significant contents of NBOs, i.e. at a high alkali content [7,10–12].

Isostatic pressurization above the glass transition temperature only weakly increases the fraction of tetrahedral coordinated boron in soda–lime–borate glasses, i.e. by ~2.5% from 0.1 to 600 MPa [13]. Consistent with these findings in pure B₂O₃ glass the increase of (B^{IV}) upon pressurization to 6 GPa is 27% [9]. It has been found that relaxation of boron speciation below the ambient glass transition temperature (0.9 T_g) in compressed soda–lime–borate glasses is decoupled from changes in macroscopic glass properties such as hardness, refractive index and density [13].

In contrast to effects of temperature, pressure and network modifier almost nothing is known about the role of structural bonded water on the boron speciation. A crucial question is, whether the influence of H₂O on the borate glass structure is similar to other network modifiers, in particular alkali oxides. For silicate and aluminosilicate glasses it was

found that the effect of water and alkali oxides on melt properties such as viscosity is rather similar [14,15].

Infrared spectroscopy gives evidence that two main water species are present in the glasses: molecular water and OH-groups [16–19]. OH-groups are formed in the melt by the interaction of water molecules with the network and anhydrous bridging oxygen (BO), as represented in Eq. (2).



Accompanied with this reaction is a depolymerization of the network. Assuming ideal mixing of $\text{H}_2\text{O}_{(\text{melt})}$, $\text{O}_{(\text{melt})}$, and $\text{OH}_{(\text{melt})}$, the equilibrium constant K for Eq. (2) is

$$K = \frac{[\text{OH}]^2}{[\text{H}_2\text{O}] \cdot [\text{O}]} \quad (3)$$

where square brackets signify mole fractions on a single oxygen basis, e.g. [16,18–20]. A basic assumption for the interpretation of the data is that the measured speciation in glasses at room temperature corresponds to the equilibrium water speciation in the melt, which was frozen at T_g [21,22].

Quantification of hydrous species can be obtained with the Lambert–Beer law after measuring the peak heights of the combination of stretching and bending vibration bands of OH-groups and molecular water, respectively. Since the linear molar absorption coefficients of the bands are strongly dependent on the glass composition [23–25] and no such data for soda–lime–borate glasses is available, a calibration of near-infrared spectroscopy was performed for the different borate glasses under investigation.

Information on water speciation in water-rich glasses of technical interest are rare [26–28]. To incorporate several wt.% of water into glasses pressures in the order of several 100 MPa are required. Such high volatile contents facilitate the investigation of water-related processes such as diffusion and relaxation mechanisms or the study of glass properties as density, elastic moduli, refractive index, crack initiation probability, and hardness.

2. Experimental and analytical methods

2.1. Starting materials

The three soda–lime–borate glasses with nominal compositions NCBx ($x = 5, 15$ and 25), corresponding to $x\text{Na}_2\text{O}$, 10CaO , $90 - x\text{B}_2\text{O}_3$ (in mol%), were prepared from Na_2CO_3 , CaCO_3 and H_3BO_3 powders. The mixtures were melted at 1373 K for only 10 min in a covered Pt-crucible in order to avoid loss of alkalis or boron during the high temperature dwell. Improved glass homogeneity was achieved by crushing the glass and subsequent repeated melting. By quenching the melts in air on a brass plate clear glass products were produced.

The composition and the homogeneity of the glasses was analyzed by electron microprobe analyses (EMPA). On each glass sample 60–100 analyses were performed using a Cameca SX-100 microprobe. Only the Na_2O and CaO contents could be measured with the microprobe, because boron is too light for this method. In the case of EMPA measurements, the B_2O_3 content of the glasses was estimated by a difference of the total of measured oxides to 100 wt.%. Measurement conditions included a beam current of 15 nA, acceleration voltage of 15 kV, defocused beam of 5 μm spot size, and counting times of 10 to 20 s. The programmed matrix correction “PAP” according to Pouchou and Pichoir [29], was used to correct the measured oxide content. To verify the by-difference estimation of the boron content, inductively coupled plasma optical emission spectroscopy (ICP-OES, 715-ES VARIAN) was used. From each starting material ~100 mg was dissolved by microwave digestion using 3 ml of 65% HNO_3 and 2 ml of H_2O .

The compositions of the glasses were analyzed by the inductively coupled plasma optical emission spectroscopy (ICP-OES, 715-ES VARIAN). From each starting material ~100 mg was dissolved by microwave digestion using 3 ml 65% HNO_3 and 2 ml H_2O . The ICP-OES analyses of the sodium and calcium contents were verified using electron microprobe analyses (EMPA). On each glass sample 60–100 analyses were performed using the Cameca SX-100 microprobe. Only the Na_2O and CaO contents could be measured with the microprobe, because boron is too light for this method. In the case of EMPA measurements, the B_2O_3 content of the glasses was estimated by difference of the total of measured oxides to 100 wt.%. Measurement conditions included a beam current of 15 nA, acceleration voltage of 15 kV, defocused beam of 5 μm spot size, and counting times of 10 to 20 s. The programmed matrix correction “PAP” according to Pouchou and Pichoir [29], was used to correct the measured oxide content. The concentrations of sodium, calcium and boron oxides are given in Table 1. A good agreement between the analysis obtained by ICP-OES and EMPA was obtained (Table 1).

2.2. Hydrous and compressed glasses

For syntheses of hydrous glasses containing up to 8 wt.%, glass powder and distilled water were filled stepwise in turn in a platinum capsule (diameter: 6 mm, length: 25–30 mm) to facilitate homogeneous distribution of water in the glass. To produce anhydrous compressed glasses only the starting glass powders were loaded into platinum capsules. By subsequent compaction of the material in the capsule using a steel piston a cylindrical shape of glass bodies was achieved. After sealing the capsules with a PUK welding device (PUK³ Professional Plus, Co. Lampert), possible weight loss due to a leakage were checked by placing the capsules in a drying furnace at 373 K.

All syntheses were performed in an internally heated pressure vessel (IHPV) at 500 MPa and 1423 K for 14–20 h using argon as pressure medium. A detailed description of the apparatus is given in Berndt et al. [30]. For all syntheses similar pressure was chosen to eliminate pressure induced differences in the glass structure and properties. For each run two capsules were placed in the hot spot of the sample holder between the two furnace-controlling K-type thermocouples (Ni-CrNi). The temperature of the samples was controlled by a third thermocouple located in the middle of the hot spot zone. The maximum variation in temperature was ± 10 °C and pressure accuracy is within ± 50 bars. In order to preserve pressure-induced structural changes and to avoid water loss of the glasses, samples were isobarically quenched (by switching of the furnace) using an automatic pressure controller. This leads to a cooling rate of ~200 K min^{-1} through the glass transition range.

All glass cylinders after high pressure synthesis were clear and no crystals or bubbles could be observed. For IR and KFT measurements glass pieces were cut from each end of the glass body to test the homogeneous distribution of water (Table 2). Exposure to water was avoided and oil was used for sawing and polishing of the samples, e.g. for preparation of thin-sections. All samples were stored in a desiccator with P_2O_5 as desiccant.

Table 1
Chemical composition of starting material of soda–lime–borate glasses oxide in mol% normalized to 100.

	Na_2O	CaO	B_2O_3	
NCB5	5.42	10.24	84.34	OES
	5.57 (0.35)	10.06 (0.24)	84.37 ^a	EMPA
NCB15	15.26	10.04	74.71	OES
	15.18 (0.54)	10.33 (0.28)	74.49 [*]	EMPA
NCB25	24.9	9.95	65.15	OES
	25.96 (0.61)	10.37 (0.25)	63.66 [*]	EMPA

Notes. EMPA analyses are based on 100 measurements (NCB5 and NCB25) and 60 measurements (NCB15). 1 standard deviation is given in parentheses.

^a Boron oxide content is calculated by difference based on Na_2O and CaO contents. OES data are based on single measurements.

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