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H_2O speciation in float glass and soda lime silica glass

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Abstract

The speciation of H_2O in float glass (FG) and soda lime silica glass (SLS) was investigated using IR and NMR spectroscopy. Molar absorption coefficients for the near-infrared (NIR) combination bands at 4500 and 5200 cm^{-1}, assigned to OH groups and H_2O molecules, respectively, were determined using hydrated glasses containing 0.5–7.4 wt.% of dissolved H_2O. Water contents of the samples used in the calibration were determined by Karl–Fischer titration or mid-infrared spectroscopy. Different combinations of baseline corrections and intensity measures were applied to evaluate the NIR spectra with tangent baselines and measurement of peak heights giving the best reproducibility. Deviations up to 30% relative were observed between water species concentrations determined by NIR spectroscopy using an internally consistent calibration based on bulk water content and those determined by low temperature static ^1H NMR spectroscopy. This implies that the assumption of constant NIR absorption coefficients may be not valid for glasses in which dissolved water is strongly hydrogen-bonded. Based on the NMR data the NIR absorption coefficients were re-calibrated, demonstrating that in particular the absorption coefficient for the band at 4500 cm^{-1} (ε_{4500}) varies with water content. For float glass ε_{4500} grows by 35% when the water content increases from 0.5 to 4.0 wt.%. An opposite trend was found for soda lime glass with an approximately linear decrease of ε_{4500} by 27% relative between 0.5 and 7.5 wt.% H_2O. For the 5200 cm^{-1} band we could not resolve a dependence of the absorption coefficient (ε_{5200}) on water content (values of 0.89 ± 0.06 and 0.95 ± 0.06 L mol^{-1} cm^{-1} were determined for FG and SLS glass, respectively). However, this may be a consequence of the low precision in determining of ε_{5200} at water contents below 2 wt.%. Based on the improved NIR calibrations, the OH concentrations at given water content are typically lower in FG than in SLS glasses with apparent saturation values of 1.4 wt.% (FG) and 2.2 wt.% (SLS) of water dissolved as OH groups. The difference in OH contents could be related to the different chemical compositions of these two glasses, in particular the concentration of alkaline-earth elements and the ratio of Mg/Ca, which are larger in FG glass than in SLS glass. Using the new water speciation data, we have re-evaluated the molar absorption coefficient for the H_2O bending vibration band at 1630 cm^{-1}.

Keywords: IR spectroscopy; Float glass; Soda lime silica glass; H_2O speciation; NMR spectroscopy; Absorption coefficients

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1. Introduction

Infrared spectroscopy is a well established technique to quantify dissolved water in industrial and natural glasses. As shown by near-infrared (NIR) and nuclear magnetic resonance (NMR) spectroscopy, water dissolves in silicate glasses as OH groups and H_2O molecules (Scholze, 1960; Bartholomew and Schreurs, 1980; Stolper, 1982a,b; Eckert et al., 1988; Schmidt et al., 2001). In silicate glasses OH groups are usually bonded to silicon (Kohn et al., 1989; Zotov and Keppler, 1998; Robert et al., 2001), but recent NMR findings give evidence that additionally free OH− ions are linked to Mg and Ca in alkaline earth silicates (Xue and Kanzaki, 2004). In aluminosilicate glasses OH groups may also form bridges between two tetrahedral cations (Kohn et al., 1989). The interconversion of OH groups and H_2O molecules can be described with the reaction

$$H_2O + O \Leftrightarrow 2OH \quad (1)$$

where O is an anhydrous oxygen. Assuming ideal mixing of the H_2O, O and OH, the equilibrium constant K_{ws} for reaction (1) is given by

$$K_{ws} = \frac{[OH]^2}{[H_2O] \cdot [O]} \quad (2)$$

where square brackets refer to mole fractions calculated on a single oxygen basis. At low water contents, which are typically found in technical glasses, OH groups are predominant and molecular H_2O concentration is often below the detection limit. With increasing water content the relative abundance of H_2O molecules grows and it becomes the dominant species above 3–6 wt.% H_2O_t (hereafter the term H_2O_t is used for the total water content whereas H_2O refers to water incorporated in molecular form), depending on glass composition and cooling rate (Silver et al., 1990; Behrens et al., 1996; Zhang et al., 1997; Behrens and Nowak, 2003).

The hydrous species are assumed to have different effects on the structure and properties of silicate glasses and melts. The formation of OH groups results in depolymerization and weakening of the silicate network (Scholze, 1960; Stolper, 1982a,b; Kohn et al., 1989). As a consequence, the viscosity of melts is strongly reduced (Persikov et al., 1990; Hess and Dingwell, 1996; Richet et al., 1996; Schulze et al., 1996; Romano et al., 2001; Giordano and Dingwell, 2003; Giordano et al., 2004; Whittington et al., 2004) and the diffusivity of melt components is strongly enhanced (Baker, 1991; Watson, 1994; Koepke and Behrens, 2001). Additionally, the electrical conductivity of the glasses may increase due to contributions of proton hopping from OH groups to neighboring non-bridging oxygen (Behrens et al., 2002). H_2O molecules, on the other hand, play an important role in water diffusion and degassing of silicate melts (Zhang et al., 1991; Watson, 1994).

Specific absorption bands for OH groups and H_2O molecules are observed in the near-infrared domain at ~4500 and ~5200 cm^{-1}, respectively, which can be used for quantitative determination of species concentrations (Scholze, 1960; Bartholomew et al., 1980; Stolper, 1982a,b). Knowledge of the density of the sample and the molar absorption coefficient is required for the evaluation of the near-infrared spectra. These properties strongly depend on anhydrous glass composition (Silver et al., 1990; Behrens et al., 1996; Richet et al., 2000; Ohlhorst et al., 2001).

Most of previous NIR spectroscopic studies were focused on aluminosilicate glasses with weak or negligible hydrogen bonding as indicated by the simple asymmetric OH stretching vibration band near 3500 cm^{-1} (Stolper, 1982a,b; Silver et al., 1990; Dixon et al., 1995; Behrens et al., 1996; Zhang et al., 1997; Withers and Behrens, 1999; Yamashita et al., 1999; Ohlhorst et al., 2001; Schmidt et al., 2001; Mandeville et al., 2002). For these glasses it has been generally assumed that the absorption coefficients for the NIR bands are independent of water content. Support for this assumption is given by the good agreement between NIR and static ^1H NMR spectroscopic determinations of hydrous species in various alkali aluminosilicates (Schmidt et al., 2001). However, the assumption of constant absorption coefficients may not be generally valid. Zhang et al. (1997) found indications of the variation of absorption coefficients with water content for hydrous rhyolitic glasses with water contents below 2.4 wt.%. A general trend of an increasing absorption coefficient for the 4500 cm^{-1} band with increasing water content was observed by Peuker et al. (2003) for various silicate and aluminosilicate glasses, including several glasses with pronounced hydrogen bonding.

The observed differences in variation of absorption coefficients with water content may be related to the ranges of water content used in the studies (variations have been observed at relatively low water contents) and the procedures used for spectra evaluation. A general problem is that an independent confirmation of species concentration by another method is often missing and absorption coefficients are based only on an internally consistent calibration using bulk water determinations.

Here we present a systematic calibration of molar absorption coefficients for the NIR bands of hydrous species in float glass and soda lime silica glass. A large