

**LETTER**

The 4500 cm$^{-1}$ infrared absorption band in hydrous aluminosilicate glasses is a combination band of the fundamental (Si,Al)-OH and O-H vibrations

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**ABSTRACT**

The position of the infrared absorption band near 4500 cm$^{-1}$ shifts from 4520 to 4440 cm$^{-1}$ as the Al content increases along the SiO$_2$-NaAlSiO$_3$ join and closely follows the sum of the positions of the Raman bands near 900 and 3600 cm$^{-1}$. This confirms the idea that the 4500 cm$^{-1}$ band is a combination band of the fundamental (Si,Al)-OH vibration near 900 cm$^{-1}$ and the fundamental O-H stretching vibration near 3600 cm$^{-1}$. As a consequence, the 4500 cm$^{-1}$ band should not be used to quantify the water speciation for glass compositions for which significant amounts of free hydroxyls are expected as these do not contribute to the band’s intensity.

**Keywords:** Raman spectroscopy, infrared spectroscopy, FTIR, water speciation, silicate glasses, band assignment

**INTRODUCTION**

Intense spectroscopic study has established that water is present in silicate glasses and melts as both hydroxyl groups (OH) and molecular water (H$_2$O$_{mol}$) and the Earth science community has devoted substantial efforts to quantify this speciation as a function of anhydrous composition, water content, and temperature (Behrens and Gaillard 2006). Although static, low-temperature $^1$H NMR spectroscopy has been applied successfully to the quantification of the water speciation in bulk glass samples (Schmidt et al. 2001), infrared spectroscopy remains the only widely accepted method for the analysis of the water speciation in glasses and melts at high spatial resolution or high temperature or pressure.

The quantification of the infrared spectroscopic data usually depends on an internally consistent calibration of the molar absorption coefficients of the combination bands near 4500 and 5200 cm$^{-1}$ (Bartholomew et al. 1980; Scholze 1966; Stolper 1982). Whereas the band near 5200 cm$^{-1}$ can be confidently assigned to a combination band of the fundamental O-H stretching vibration (ca. 3600 cm$^{-1}$) and the fundamental H-O-H bending vibration within molecular H$_2$O (ca. 1600 cm$^{-1}$), the assignment of the band near 4500 cm$^{-1}$ is not yet clear, despite its widespread use for quantification purposes. The band can be assigned to a combination band of the fundamental O-H stretching vibration (ca. 3600 cm$^{-1}$) and some vibration of the OH groups in the 900–1000 cm$^{-1}$ range (Scholze 1966). One obvious candidate is the vibration around 900 cm$^{-1}$, which is present in both the infrared absorption (Silver and Stolper 1989) and Raman spectra (McMillan et al. 1993; Mysen et al. 1980) of hydrous albite glass, but absent for the anhydrous glass.

The goal of this study is to verify whether the 4500 cm$^{-1}$ band is indeed the combination band of the 3600 and 900 cm$^{-1}$ vibrations. To test this hypothesis, infrared absorption and Raman spectra were collected for a series of hydrous glasses along the SiO$_2$-NaAlSiO$_3$ join. Relatively low water contents ($\leq$1 wt% H$_2$O) were used to reduce the contribution of H$_2$O$_{mol}$ to the spectra.

**EXPERIMENTAL METHODS**

The studied samples are part of a sample set studied by NMR spectroscopy (Malfait and Xue, submitted). Six anhydrous glasses along the SiO$_2$-NaAlSiO$_3$ join were prepared by mixing the appropriate proportions of SiO$_2$, Al$_2$O$_3$, and Na$_2$CO$_3$. After decarbonation, the samples were melted in 5 g batches at temperatures from 1833 to 1893 K for 40 to 105 min and quenched to glass by dipping the bottom of the Pt crucible in water. The compositions, measured by electron microprobe, agree with the target compositions within 1 wt%. Hydrous glasses were prepared by loading 100 mg of anhydrous glass and deionized water into Pt capsules (3 mm o.d., 2 cm long). The welded capsules were suspended from a Mo wire in the hot zone of an internally heated pressure vessel and isobarically quenched by dropping the capsules to the cold zone of the pressure vessel (ca. 333 K, estimated quench rate: 200–500 K/s). Run conditions were 1773 K and 200 MPa for 4 h. The water content of the recovered glasses was measured by quantitative $^1$H NMR and by infrared spectroscopy for those compositions for which the molar absorption coefficients are known (Behrens et al. 1996; Silver et al. 1990); the results are listed in Table 1.

Near infrared absorption spectra were acquired in transmission mode from double polished sections (0.4–0.9 mm thick) with a Jasco micro-FTIR spectrometer. Spectra were acquired with 100 scans from a 100 × 100 µm area. Spectra from different parts of the samples were identical within the noise.

Unpolarized Raman spectra were collected in backscatter geometry for 5 × 60 s. The 488 nm line of an Ar laser was used for excitation, with a power of ca. 30 mW, measured at the sample surface. An imaging monochromator with a focal length of 500 mm, a grating of 1200 gr/mm and a liquid-nitrogen-cooled CCD detector were used. Spectra were acquired for three spectral windows spanning the range of 100 to 3800 cm$^{-1}$. The Raman shift was calibrated using the plasma lines of the laser and spikes were removed automatically by a gradient-based algorithm.

**RESULTS**

The infrared absorption spectra for different Al contents are shown in Figure 1; the peak positions and the OH/H$_2$O$_{mol}$ speciation, for the compositions for which molar absorption

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