Molar absorptivities of OH and H₂O in rhyolitic glass at room temperature and at 400–600 °C

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ABSTRACT

We determined near-infrared (NIR) molar absorptivities of hydroxyl group (4500 cm⁻¹) and molecular water (5230 cm⁻¹) in rhyolitic glasses at room temperature and at high temperature, 400–600 °C. Five rhyolitic glasses with 0.5–2.8 wt% total water were analyzed by FT-IR microspectroscopy at room temperature and at 50 °C intervals in the range of 400 to 600 °C using a heating stage. The total water contents in the rhyolitic glasses were measured by Karl-Fischer titration. Based on these data, the linear molar absorptivities of the 4500 and 5230 cm⁻¹ bands at room temperature were determined to be 1.42 ± 0.12 and 1.75 ± 0.08 L/mol·cm, respectively. The integral molar absorptivities obtained are 285 ± 24 and 239 ± 11 L/mol·cm² for the 4500 and 5230 cm⁻¹ bands, respectively. These values can be used to determine the concentrations of hydroxyl group and molecular water in rhyolitic glass with 0.5–2.8 wt% total water at room temperature. The experimental results at high temperature show that the linear and integral molar absorptivities of the 4500 cm⁻¹ band at 400–600 °C generally remain within 6% of the values at room temperature. On the other hand, the linear and integral molar absorptivities of the 5230 cm⁻¹ band systematically decrease with increasing temperature in the ranges of 400 to 600 °C. These high-temperature molar absorptivities are useful for evaluating the water speciation in rhyolitic glass by in situ high-temperature IR microspectroscopy.

INTRODUCTION

It is known that two water species, hydroxyl group (OH) and molecular water (H₂Oₙ), occur in silicate melts and glasses. Determining the concentrations of these water species (OH and H₂Oₙ) in natural and synthetic glasses is essential to reveal: (1) the water solubility and dissolution mechanisms of water into silicate melts and glasses; (2) the thermodynamic properties of hydrous melt; (3) the dependence of the physical properties (viscosity and density) of silicate melts and glasses on water content; and (4) the diffusion and reaction processes of water species in silicate melts and glasses.

Infrared (IR) spectroscopy is a powerful tool for determining the concentrations of water species in natural and synthetic glasses at room temperature. In this technique, the concentrations of water species are determined from intensities of the absorption bands corresponding to water species and the molar absorptivities that have been calibrated by many authors (e.g., Stolper 1982; Newman et al. 1986; Dobson et al. 1989; Ihinger et al. 1994; Dixon et al. 1995; Yamashita et al. 1997; Ohlhorst et al. 2001; Okumura et al. 2003). By previous IR spectroscopic studies (e.g., Stolper 1982, 1989; Zhang et al. 1997; Ihinger et al. 1999), it was revealed that the main water species was OH at low total water contents, but the contribution of H₂Oₙ increased with the total water content, and that the OH content increased with temperature at a certain total water content.

High-temperature IR studies also have been conducted using the heating stage, diamond cell, and sapphire cell coupled to IR spectroscopy (e.g., Kepler and Bagdassarov 1993; Nowak and Behrens 1995; Shen and Keppler 1995; Withers et al. 1999; Nowak and Behrens 2001; Okumura and Nakashima 2004). Because the in situ IR technique directly measures the absorptions that are proportional to the concentrations of water species at high temperature, it has large advantages over IR spectroscopy at room temperature for investigating water speciation in silicate melts and glasses at high temperature. In particular, the in situ IR technique can avoid the relaxation of water speciation during sample cooling. Therefore, the in situ IR technique is useful for estimating the equilibrium water speciation at high temperature with a diamond cell and a sapphire cell (Nowak and Behrens 1995; Shen and Keppler 1995; Nowak and Behrens 2001), and for investigating the diffusion and reaction processes of water species at high temperature with a heating stage (Okumura and Nakashima 2004). Here it should be noted that investigation of the equilibrium water speciation by the in situ technique might be complicated due to the slow relaxation of water species at low temperature (e.g., Dingwell and Webb 1990; Zhang et al. 1995) and the formation of submicrometer bubbles at low pressure (Behrens and Nowak 2003).

A disadvantage in the in situ technique is a lack of calibration data for high-temperature molar absorptivity. Only a few studies (Sowerby and Keppler 1999; Withers et al. 1999; Nowak and Behrens 2001) have evaluated high-temperature molar absorptivities of OH and H₂Oₙ. It is difficult to determine high-temperature molar absorptivities by comparing the IR band intensities at high...