AMORPHOUS MATERIALS: PROPERTIES, STRUCTURE, AND DURABILITY†
Quantitative Raman spectroscopy: Speciation of Na-silicate glasses and melts

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ABSTRACT

In situ, high-temperature Raman spectroscopy was used to study the $Q^n$ speciation in binary Na-silicate glasses and melts. Over 300 Raman spectra in the compositional range from 25 to 40 mol% $Na_2O$ were collected at room and high temperatures between 800 and 1200 K. Quantitative information on the relative abundances of species in melts was obtained from the Raman spectra through a quantification procedure that does not require any a priori assumptions about the line shapes or external calibration of the Raman scattering efficiencies for the various $Q^n$ species. The $\Delta H^\circ$ associated with the speciation reaction $2Q^2 = Q^3 + Q^1$ was found to be $20.3 \pm 7.9 \text{ kJ/mol}$. For a given temperature, the speciation is more disordered in sodium than in potassium silicate melts. Because of the smaller temperature dependence of the speciation in the sodium silicate system, the difference in the speciation for the sodium and potassium silicate system decreases with increasing temperature. In addition to the speciation data, the partial Raman spectra for the different species were obtained. The experimentally observed variation of the partial Raman spectra with temperature, and, to a minor extent, with composition, should stimulate future theoretical studies on the vibrational properties of silicate glasses and melts.

Keywords: Silicate melts, Na-silicate glasses, speciation, Raman spectroscopy, partial Raman spectra

INTRODUCTION

The physical properties of magmas, e.g., viscosity, heat capacity, and density, are mostly determined by the properties of the silicate-melt phase. Thus, silicate melts play an essential role in the mass and heat transfer in the earth and terrestrial planets. In addition, detailed knowledge of silicate-melt properties is indispensable for a better understanding of volcanic and magmatic processes. Because of this, the earth science community has invested considerable effort in measuring the bulk properties of silicate glasses and melts. Due to the limited composition-temperature-pressure range over which these properties can be measured, a tool to predict these properties is desired. To achieve this, a fundamental knowledge about the factors governing these properties is required. Several decades of intense spectroscopic and diffraction studies have demonstrated that the short- and medium-range order of silicate glasses and melts strongly influences their bulk properties (e.g., Lee and Stebbins 2002; McMillan and Wolf 1995; Mysen and Richet 2005; Mysen 2006; Navrotsky 1995; Stebbins et al. 1995a and references therein). For example, in the $K_2O-SiO_2$ system, non-linear variations of the glass transition temperatures can be explained by the entropy of mixing of the silicate species; the anomalous heat capacity behavior is caused by the presence of numerous three-membered rings (Malfait et al. 2007a).

The structure of silicate melts and glasses at atmospheric pressure consists of a three-dimensional network of $SiO_4$ tetrahedra linked by bridging O atoms (BO) and addition of network-modifying cation oxides breaks up this network by generating non-bridging O atoms (NBO) (e.g., Brawer and White 1975; Masson 1977). The short-range structure of silicate glasses and melts can be described through the abundance of the different $Q^n$ species, where $Q$ represents a $SiO_4$ tetrahedron and $n$ is the number of bridging O atoms. The abundance of these $Q^n$ species is controlled by the following speciation reactions:

$$2Q^n = Q^{n+1} + Q^{n-1} \quad (n = 3, 2, 1). \quad (1)$$

Assuming that the activity coefficients cancel out in the speciation reaction, the equilibrium constants $K_n$ of reaction 1 are

$$K_n = \frac{[Q^{n-1}][Q^{n+1}]}{[Q^n]^2} \quad (2)$$

where $[Q^n]$ represents the abundance of the species.

Previous studies have linked the $Q^n$ speciation to the configurational heat capacity (Brandriss and Stebbins 1988), mineral-melt equilibria (Halter and Mysen 2004), and melt rheology (Malfait and Halter 2008; Malfait et al. 2007a). Room-temperature $^{29}Si$ NMR measurements on binary silicate glasses with different types of modifier cations have shown that the