Coordination of Ti$^{4+}$ in silicate glasses: A high-resolution XANES spectroscopy study at the Ti K edge

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ABSTRACT

The coordination environment of Ti in eight Ti-bearing glasses of the Na$_2$SiO$_3$-Na$_2$Ti$_2$O$_5$ join (NTS) and in six ATY$_2$ glasses (A$_2$O-TiO$_2$, with A = Na, K, or Rb and Y = Si or Ge) was determined using high-resolution, X-ray absorption near-edge structure (XANES) spectroscopy at the Ti K edge in ambient conditions.

Fivefold-coordinated Ti ($^{5\text{f}}$Ti) is the dominant Ti species ($\approx 50 \pm 10\%$ of the total Ti) in all the glasses studied. Sixfold-coordinated Ti was detected mostly in sodic glasses (NTS, NTS2, NTG2), and it increases with TiO$_2$ content (as high as 40 $\pm 10\%$ of the total of Ti in the most TiO$_2$-rich NTS glasses) and in the order Si $<$ Ge. Fourfold-coordinated Ti was detected only in non sodic ATY$_2$ glasses, and its content increases in the order Na $<$ K $<$ Rb and Ge $<$ Si. Fivefold-coordinated Ti$^{4+}$ is probably present as square pyramidal, titanyl-bearing moieties, or ($^{5\text{f}}$Ti=O)$_2$O$_3$.

A synthesis of Ti$^{4+}$ coordination for oxide glasses derived using direct methods (X-ray absorption and neutron scattering) can be used, for instance, to help in the interpretation of Raman scattering spectra collected for Ti-bearing glasses and to estimate NBO/T ratios better for titanosilicate glasses and melts.

INTRODUCTION

The coordination chemistry of Ti$^{4+}$ in silicate glasses and melts has recently received particular attention because of unusual variations in some of the physical properties of these systems, such as density, shear viscosity, and heat capacity (Richet and Bottinga 1985; Myssen 1988; Hess 1991; Dingwell 1992a, 1992b; Lange and Navrotsky 1993; Bouhifd 1995). However, because of the existence of several coordinations around Ti$^{4+}$ in oxide compounds ($^{4\text{f}}$Ti, $^{5\text{f}}$Ti, and $^{6\text{f}}$Ti), the coordination of Ti$^{4+}$ in titanosilicate glasses and melts may also vary extensively. However, the coordination chemistry of Ti$^{4+}$ in oxide glasses is still not well understood. This is due to a lack of accurate direct structural information, despite the many Raman scattering, X-ray absorption, X-ray scattering, X-ray photoemission, and neutron scattering studies that have been published (see Farges et al. 1996a, and references therein).

Among these techniques, X-ray absorption fine-structure (XAFS) methods [which include X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine-structure (EXAFS) spectroscopies] are direct structural probes that are element specific. Therefore, they are the tools of choice for the direct determination of the coordination environment of Ti$^{4+}$ in amorphous materials. Unfortunately, most of the past XAFS studies on the coordination of Ti in glasses were based on a nonrepresentative set of Ti-bearing model compounds (few, if any, model compounds contained $^{4\text{f}}$Ti and $^{5\text{f}}$Ti). Also, the possible existence of $^{5\text{f}}$Ti and various mixtures of Ti coordination (and how these mixtures affect preedge features) has long been ignored or considered only briefly. Finally, many preedge spectra have been collected under low-resolution conditions, which resulted in less accurate structural information. Therefore, several previous interpretations of XAFS spectra must be revisited using more comprehensive preedge information.

In an attempt to alleviate these limitations, a large selection of Ti-bearing model compounds has recently been studied by XANES spectroscopy, thanks to the collection of a large set of high-resolution XANES data and the ab-initio calculation of XANES spectra (Farges et al. 1996a). By using this new method for XANES interpretation, these authors were able to demonstrate the importance of square pyramidal $^{5\text{f}}$Ti$^{4+}$ species in several Ti-bearing silicate glasses and melts, synthetic and natural (Farges 1996; Farges et al. 1996b; Farges and Brown 1997). However, no systematic high-resolution preedge study of the coordination environment of Ti has yet been conducted for oxide glasses of similar composition or structure (such as along a specific join, etc.).

In this paper, high-resolution XANES spectroscopy is used to characterize the local structure around Ti$^{4+}$ in two sets of Ti-bearing silicate glasses. One set consists of eight glasses within the Na$_2$SiO$_3$-Na$_2$Ti$_2$O$_5$ join (NTS), and the second set contains six glasses of composition A$_2$O-TiO$_2$,2YO$_2$ (ATY$_2$), where A = Na, K, or Rb and Y = Si or Ge. In the first set of glasses, the calculated num-