

Effect of aluminum on Ti-coordination in silicate glasses: A XANES study

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ABSTRACT

The structure of glasses in the $K_2O-Al_2O_3-TiO_2-SiO_2$ system was investigated using XANES spectroscopy. Glass samples, synthesized by quenching in air from high temperature fusions, represent the addition of Al_2O_3 to a base of composition $K_2TiSi_4O_{11}$ in amounts corresponding to 0.25, 0.50, 0.75, 1.00, 1.25, and 1.50 mol p.f.u. In the Ti-free system, this range of alkali/aluminum ratios crosses the leucite stoichiometry at 1.0. Si K-edge and Al K-edge spectra indicate tetrahedral environments for these elements, and show no variations related to coordination change as a function of Al content. Changes in the relative intensities of peaks in the Al K-edge, however, suggest variation in the intertetrahedral (T-O-T) angle. We associate the decrease of this angle for the glasses of peraluminous composition with the presence of triclusters of tetrahedra. The pre-edge peak absorption features in the Ti K-edge XANES spectra indicate that the average Ti coordination decreases with the addition of Al_2O_3 . We infer depletion of fivefold-coordinated titanium (possibly as alkali titanyl complexes), which are dominant in the Al-free glass, by the formation of fourfold coordinated Ti and alkali aluminate complexes (up to a concentration of 40% in the most peraluminous glass). Significant amounts of ^{IV}Ti remain present, even at peraluminous compositions, in further support of tricluster formation as a mechanism for Al incorporation.