

Hydrogen Speciation in Synthetic Quartz and Its Relevance to Hydrolytic Weakening

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Hydrothermally-grown synthetic quartz crystals generally display a far lower plastic yield strength than colorless and clear vug-grown natural quartz crystal. It is of interest, therefore, to characterize the nature of the incorporation of hydrogen in these weak crystals. Previous infrared and Raman spectroscopy has focused on the absorptions due to the O-H stretching mode at wavelengths near 3 μm but these absorptions are not diagnostic of the mode of hydrogen incorporation. We have examined a suite of Bell Laboratories synthetic quartz grown in 0.5-1.0 M NaOH at 338-377°C and fluid pressures of 138-281 MPa. Using near-infrared spectroscopy, we were able to discriminate between hydrogen incorporated as molecular water (H-O-H) or as hydroxyl (X-O-H where X \neq H) by measuring the combination bend-stretch absorptions. We conclude that the dominant speciation of hydrogen is as molecular water in clusters of less than a few hundred molecules. Cluster sizes greater than this are ruled out by the lack of ice bands in spectra taken at 77 K and solitary molecules caged by the structure seem to be ruled out by the lack of anisotropy in absorption and by breadth of the 3 μm absorption peak. Individual $\text{H}_4\text{O}_4^{4-}$ tetrahedral groups substituting for silica tetrahedra are ruled out because these should be expressed as Si-O-H bend-stretch bands, which are only a minor component of the near-infrared spectra. Increasing uptake of molecular water with increasing growth rate and variations in uptake with growth direction indicate that molecular water incorporation in synthetic quartz is a nonequilibrium process. Sodium concentrations increase with increasing molecular water concentrations with a ratio of five water molecules to one sodium atom. These results indicate that molecular water as a reactant proposed by Griggs and Blacic in the weakening hydrolysis reaction exists in weak synthetic quartz but that hydrolyzed Si-O bonds can only be a minor component of the total hydrogen concentration in the starting material.