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Simultaneous aluminum, silicon, and sodium coordination changes in 6 GPa sodium aluminosilicate glasses

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Abstract

We present the first direct observation of high-coordinated Si and Al occurring together in a series of high-pressure sodium aluminosilicate glasses, quenched from melts at 6 GPa. Using ^{29}Si MAS NMR, we observe that a small amount of Al does not have a significant effect on the amount of ^{V}Si or ^{VI}Si generated, but that larger Al concentrations lead to a gradual decrease in both these species. ^{27}Al MAS NMR spectra show that samples with small amounts of Al have extremely high mean Al coordination values of up to 5.49, but that larger Al concentrations cause a gradual decrease in both ^{V}Al and ^{VI}Al. Although mean Al and Si coordination numbers both decrease with increasing Al contents, the weighted combined (Al+Si) coordination number increases. Silicon and Al resonances shift in frequency with increasing pressure or changing Al concentration, indicating additional structural changes, including compression of network bond angles. Increases in the ^{23}Na isotropic chemical shifts indicate decreases in the mean Na-O bond lengths with increasing pressure, which are more dramatic at higher Al contents. Recovered glass densities are about 10 to 15% greater than those of similar ambient pressure samples. However, the density increases due to the combined coordination changes of Al and Si are estimated to total only about 1 to 2%, and are roughly constant with composition despite the large effects of Al content on the individual coordinations of the two cations. Thus, effects of other structural changes must be significant to the overall densification. Apparent equilibrium constants for reactions involving the generation of high-coordinated species show systematic behavior, which suggests an internal consistency to the observed Si and Al coordination number shifts.

Keywords: NMR, aluminosilicate, glass, high pressure, coordination, aluminum, silicon, sodium