Network polymerization of sulfur-bearing sodium silicate glasses by 29Si MAS NMR

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The effect of sulfur on a sodium silicate glass network was studied by 29Si magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR). Samples were prepared from reagent grade Na2CO3 and SiO2. Mixed starting materials (Na2O(40)SiO2(60) and Na2O(30)SiO2(70)) were carefully melted in Pt crucible at 1000C for 6hr. Then the samples were quenched in water. All samples were clear. We added 0.2 wt. % Gd2O3 in all glasses to reduce the relaxation time of 29Si nuclei. The silicate glass and native sulfur were well mixed and sealed in an Au capsule with graphite powder. The glass samples were quenched at pressure (below 2kbar) in an Ar-mediated internally heated pressure vessel with rapid quenching device at Tokyo Institute of Technology (SMC-2000). We made MAS NMR measurements with a Varian VXR-400S spectrometer and a MAS probe at a Larmor resonance frequency of 79.537 and 105.902 MHz for 29Si and 23Na respectively. An external standard of tetramethyl silane (TMS) for 29Si.

As for the Na2O(40)SiO2(60) (no-sulfur vs. sulfur-bearing) compositions, the broad-line 29Si NMR spectra consist of mainly two peaks by Q2 and Q3. However, the ratio of Q2 in the sulfur-bearing glass is clearly lower than that in the no-sulfur glass. As for Na2O(30)SiO2(70) compositions, 29Si NMR spectrums consist of mainly two peaks by Q3 and Q4. However, the ratio of Q3 in the sulfur-bearing glass is clearly lower than that in the no-sulfur glass. The dissolved mechanism of sulfur in silicate melts is described by the following reaction;

4SiONa (melt) + S2 = 2SiOSi (melt) + 2Na2S (melt)+ O2

The substitution of nonbridging oxygen by sulfur causes the decrease of chemical shift anisotropic feature. This result suggests that a small amount of sulfur (below 1 wt.%) cause melt polymerization.