Multiple dissolution mechanisms of sulfur into sodium silicate melts; Raman and 29Si MAS NMR spectroscopy

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Sulfur plays an important role in both geosciences and glass sciences. In a pioneering study, Fincham and Richardson (1954) suggested that sulfur is present as either sulfide or sulfate sulfur in silicate melts. However, direct spectroscopic studies on the dissolution mechanisms of sulfur into silicate melts have been limited. In this study, we have examined the states of sulfur in sulfur-bearing sodium silicate glasses (quenched melts) of a range of compositions with 29Si MAS NMR and Raman spectroscopy.

We have synthesized the sulfur-bearing glasses using starting materials of (1-x)Na2OxSiO2 (x; 0.6-1.0) glasses plus one of the following sulfur compounds: Na2S, native S, Na2S2O3, Na2SO3 and Na2SO4. These were loaded into an Au capsule, melted at 1000-1030 deg. and 2 kbar for 8 hours and then quenched to glasses in an IHPV. The native sulfur- and Na2S-doped glasses were all covered with a yellow liquid; whereas all the other glasses were homogeneous and clear.

For the (1-x)Na2OxSiO2 (x; 0.6-0.7) glasses doped with native S, Na2S2O3, Na2SO3 or Na2SO4, the Raman spectra indicate that both sodium polysulfide (Na2Sx) and sodium sulfate (Na2SO4) species are present, with the former dominant in the more reduced native sulfur-doped glasses and the latter dominant in the Na2SO4-doped glasses. Native sulfur-doped glasses of a more silica-rich composition (Na2O3SiO2) show different Raman features that may indicate a change in dissolution mechanisms of sulfur at higher silica contents.

For the Na2S-doped Na2O3SiO2 glasses, 29Si MAS NMR revealed a new peak near -60 ppm, in addition those around -80 ~ -120 ppm expected for the SiO4 groups. This peak is attributable to Si(O3S) unit according to recent ab initio calculations (Xue and Kanzaki, presentation at this meeting). The Raman spectrum for this glass shows a broad band near 350 cm-1, attributable to polysulfide, and a narrower peak near 430 cm-1. The latter has not been observed in the glasses doped with more oxidized native sulfur or Na2SO4, and could be related to Si-S linkages. The Raman spectra of Na2S-doped SiO2 glasses also contain additional peaks that may be related to similar linkages, consistent with the reported 29Si MAS NMR results for glasses synthesized from Na2S-SiO2 in open air (Asahi et al., 1998). A more systematic 29Si MAS NMR and Raman study on Na2S-doped glasses of a wider range of compositions is underway, and these results will be reported at the meeting.

In summary, our study revealed that there are a variety of dissolution mechanisms of sulfur in silicate melts depending on the oxidation state and the melt composition.