Silicate network structure in sulfate bearing Na2O-SiO2 glasses: Spectroscopic Studies by micro-Raman and 29Si MAS NMR

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The silicate network structure in sulfate bearing Na2O-SiO2 glasses has been studied with 29Si MAS NMR and micro-Raman spectroscopy.

First, Na2Si2O5 were prepared from reagent grade Na2CO3 and SiO2 at ambient pressure. Sulfate added glasses were loaded in Pt capsules, and held at 1300C and 2kbar for 9hours in an Ar-mediated IHPV.

Raman measurements were made using an ISEI-Raman system with 514.5 nm Ar-ion laser. The obtained Raman spectrum of the 1 atm Na2Si2O5 glass is identical to that reported by Furukawa et al. [4]. According to the previous work, the strong peak at 1100 cm-1 is attributed to the symmetric Si-O stretching of Q3 species. The peak at 945 cm-1 is caused by the symmetric Si-O stretching of Q2 species. In addition, the strong peak at 572 cm-1 is most likely caused by Si-O-Si bending vibration of linkages associated with the predominant Q3 species [5], on the other hand, the peak assignment of its high frequency shoulder near 600 cm-1 has been still unclear. This shoulder has often been assigned to Si-O-Si vibration of linkages associated with the Q2 species [e.g.,4], however, Matson [6] and McMillan [7] suggested that this can correspond to the symmetric oxygen breathing vibrations of three and four membered siloxane rings. As for sulfate bearing Na2Si2O5 glasses, the most novel change is the occurrence of the strong peak at 990 cm-1. This peak is S-O symmetric stretching modes from tetrahedral sulfate environment [8]. The intensity of this peak increases as increasing the amounts of sulfate. This indicates that sulfate is dissolved into silicate melts as following:

Na2SO4 (sulfate) = Na2SO4 (melt) (1)

The relative peak intensity of the 945 cm-1 to 1100 cm-1 slightly decreases as increasing the amounts of sulfate. This indicates that relative proportion of Q2 to Q3 slightly decreases as increasing sulfate content. In addition, the low frequency 572 cm-1 peak at 1 atm shifts to 580 cm-1 with increasing sulfate content, and becomes more symmetric because of the growth of its high frequency shoulder. This peak shift suggests a reduction of Si-O-Si angle of Q3, and the growth of its high frequency shoulder could be interpreted as due to increasing proportion of either Q2 species or three-membered siloxane rings.

We made MAS NMR measurements with a Varian UNITY-INOVA400NB spectrometer and a 5mm Jakobsen-type MAS probe at a Larmor resonance frequency of 79.5 MHz for 29Si. As for Na2Si2O5 glass, the 29Si MAS NMR spectrum of the starting, sulfate-free glass consists of a mainly peak attributed to Q3 species, and two shoulders on its high and low sides attributed Q2 and Q4, respectively. Whereas for the spectrum of the sulfate bearing glasses, the relative intensities of the shoulder due to Q4 species decreases compared with that of Na2Si2O5 glass. The abundances of Qn species in these glasses were calculated by fitting the spectrum with Gaussian peak shapes. The calculated results showed that the decrease of Q4 (3-4%), the increase of Q3 (3-4%) and little change of Q2. This change in Q speciation distribution was caused by decomposition of a part of added sulfate as following:

Na2SO4 (sulfate) = Na2O (melt) + SO3 (gas?) (2)

In this meeting, the more quantitative discussion of the relation between Eqn. (1) and (2) will be presented.

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