

## Silicate network structure in sulfate bearing Na<sub>2</sub>O-SiO<sub>2</sub> glasses: Spectroscopic Studies by micro-Raman and <sup>29</sup>Si MAS NMR

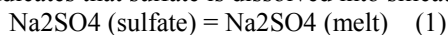
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The silicate network structure in sulfate bearing Na<sub>2</sub>O-SiO<sub>2</sub> glasses has been studied with <sup>29</sup>Si MAS NMR and micro-Raman spectroscopy.

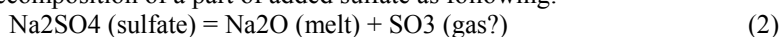
First, Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> were prepared from reagent grade Na<sub>2</sub>CO<sub>3</sub> and SiO<sub>2</sub> at ambient pressure. Sulfate added glasses were loaded in Pt capsules, and held at 1300C and 2kbar for 9hours in an Ar-mediated IHPV.

Raman measurements were made using an ISEI-Raman system with 514.5 nm Ar-ion laser. The obtained Raman spectrum of the 1 atm Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> glass is identical to that reported by Furukawa et al. [4]. According to the previous work, the strong peak at 1100 cm<sup>-1</sup> is attributed to the symmetric Si-O stretching of Q<sub>3</sub> species. The peak at 945 cm<sup>-1</sup> is caused by the symmetric Si-O stretching of Q<sub>2</sub> species. In addition, the strong peak at 572 cm<sup>-1</sup> is most likely caused by Si-O-Si bending vibration of linkages associated with the predominant Q<sub>3</sub> species [5], on the other hand, the peak assignment of its high frequency shoulder near 600 cm<sup>-1</sup> has been still unclear. This shoulder has often been assigned to Si-O-Si vibration of linkages associated with the Q<sub>2</sub> 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 Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> glasses, the most novel change is the occurrence of the strong peak at 990 cm<sup>-1</sup>. 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:



The relative peak intensity of the 945 cm<sup>-1</sup> to 1100 cm<sup>-1</sup> slightly decreases as increasing the amounts of sulfate. This indicates that relative proportion of Q<sub>2</sub> to Q<sub>3</sub> slightly decreases as increasing sulfate content. In addition, the low frequency 572 cm<sup>-1</sup> peak at 1 atm shifts to 580 cm<sup>-1</sup> 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 Q<sub>3</sub>, and the growth of its high frequency shoulder could be interpreted as due to increasing proportion of either Q<sub>2</sub> 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 <sup>29</sup>Si. As for Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> glass, the <sup>29</sup>Si MAS NMR spectrum of the starting, sulfate-free glass consists of a mainly peak attributed to Q<sub>3</sub> species, and two shoulders on its high and low sides attributed Q<sub>2</sub> and Q<sub>4</sub>, respectively. Whereas for the spectrum of the sulfate bearing glasses, the relative intensities of the shoulder due to Q<sub>4</sub> species decreases compared with that of Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> glass. The abundances of Q<sub>n</sub> species in these glasses were calculated by fitting the spectrum with Gaussian peak shapes. The calculated results showed that the decrease of Q<sub>4</sub> (3-4%), the increase of Q<sub>3</sub> (3-4%) and little change of Q<sub>2</sub>. This change in Q speciation distribution was caused by decomposition of a part of added sulfate as following:



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

### References

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