The effect of sulfate sulfur on the structure of Na_2O-SiO_2 glasses: A ^{29}Si MAS NMR, Raman and FT-IR study

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Sulfate in silicate melts plays an important role in not only volcanology but also ceramics. Here we report the relation between silicate network structure and sulfate for sodium silicate glasses (quenched melts) from ^{29}Si MAS NMR, Raman and IR studies. Sulfate-bearing glasses were prepared from mixtures of $Na_2O\cdot xSiO_2$ glasses (x = 1.5, 2, 3) and Na_2SO_4 at 1300°C and 2 kbar over 8 hours in an IHPV. The ^{29}Si MAS NMR, Raman and IR spectra of the sulfate-free glasses are consistent with those reported previously.

For all the sulfate-bearing glasses, a new peak near 980cm^{-1} in the Raman spectra appears and grows systematically with increasing Na_2SO_4 content. This peak can be attributed to the S-O stretching mode of SO_4^{2-}, confirming that Na_2SO_4 species is present in the melt.

For the $Na_2O\cdot1.5SiO_2$ composition, the ^{29}Si MAS NMR spectra indicate that the abundance of Q^2 in the sulfate-bearing glass is higher than that in the sulfate-free glass. The Raman spectra also reveal an increase in the relative height of the 945cm^{-1}(Q^2) to 1080cm^{-1}(Q^3) peak, consistent with the ^{29}Si MAS NMR result. For the $Na_2O\cdot xSiO_2$ (x = 2, 3) compositions, the ^{29}Si MAS NMR spectra indicate that the abundances of Q^4 in the sulfate-bearing glasses of different Na_2SO_4 contents are all similar, but lower than those of the sulfate-free glasses. The Raman spectra show only small changes in the relative intensities of Q^2 to Q^3, and little change near 1150cm^{-1} between the sulfate-bearing and free glasses; the assignment of the latter to Q^4 has been controversial. Thus, these data suggest that the melt structure becomes less polymerized upon Na_2SO_4 addition, possibly as a result of partial decomposition of the added Na_2SO_4 to Na_2O and SO_3.

In summary, our study suggests that sulfate largely dissolves in sodium silicate melts as Na_2SO_4 species, although some decomposes to depolymerize the melt structure.

XAFS study on trace amount of ytterbium ions incorporated in calcite and aragonite

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Trace amount of rare earth elements (REEs) induces significant effects on the crystal growth and dissolution of calcium carbonate. The substantial increase in the solubility of $CaCO_3$, the stabilization of the vaterite and the inhibition of calcite growth were caused by the addition of trace amount of lanthanum into the aqueous solutions (Tsuno et al., 2001, 2002; Kamiya et al., 2001). The uptake mechanism and chemical state of REEs incorporated into calcium carbonate are unclear. X-ray absorption fine structure (XAFS) in a fluorescence mode is practically the only method for the structural characterization of trace elements in the solid materials. In the present work, we investigated the chemical species and local structure of ytterbium (Yb) incorporated in calcite and aragonite using XANES and EXAFS technique.

Calcite was precipitated from a mixed solution of 30 mM $CaCl_2$ aq and 30 mM $NaHCO_3$ aq with a given amount of $YbCl_3$. Concentrations of Yb were 5 μM in the starting solutions. Aragonite was synthesized by adding 25 mM $MgCl_2$ into the solution as mentioned above (Kitano et al., 1962). Yb L_{III} XAFS spectra were collected in the fluorescence mode at the beamline BL-12C of the KEK-PF.

According to the XAFS results of Yb in calcite, approximately 15% Yb ion existed as divalent in the calcite, although Yb ion was trivalent in the starting solutions (Tsuno et al. 2003). Furthermore the local structure around Yb^{3+}, major Yb species in the calcite, is significantly different from that of Ca^{2+}. The coordination number of Ca ion for calcite is 6. In contrast, the nearest Yb-O coordination for Yb-doped calcite is split into two shells, the nearest 4 oxygen atoms and the second nearest 2 oxygen atoms. It was shown that localized structural relaxation occurred around Yb^{3+} which has an ionic radius smaller than Ca^{2+}. XAFS results of Yb in aragonite will be presented.

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