Geophysical Research Abstracts
Vol. 14, EGU2012-10676, 2012
EGU General Assembly 2012

Vibrational properties of silica species in MgO-SiO_2 glasses from ab initio molecular dynamics

G. Spiekermann (1), M. Steele-MacInnis (2), P.M. Kowalski (1), C. Schmidt (1), and S. Jahn (1)

(1) GFZ German Research Centre for Geosciences, Telegrafenberg, 14473 Potsdam, Germany (jahn@gfz-potsdam.de), (2) Department of Geosciences, Virginia Tech, Blacksburg VA 24061, USA

Glasses and melts in the system MgO-SiO_2 are analogs for magmas of the Earth's mantle. Therefore knowledge of the structure of these glasses and melts is important for understanding numerous geological processes. Raman spectroscopy is useful for probing the atomic-scale structure of glasses and melts. However, correct assignment of observed vibrational bands to specific structural and modal origins is challenging. We present the mode-projection technique to calculate vibrational subspectra for specific modal vibrations of several fundamental silica structures in silicate glasses. Structural subunits that we have studied include Q^0 to Q^4 tetrahedra, Si-O-Si bridging oxygen atoms for any degree of polymerization of the adjacent tetrahedra, the ethane-like symmetry of the dimer, and three- and four-fold rings. We apply this technique to ab initio molecular dynamics (MD) trajectories of MgO-SiO_2 glasses at 1000 K. We found the tetrahedral symmetric stretch at 863 cm^{-1} for Q^0, 885 cm^{-1} for Q^1, a double peak of 960 cm^{-1} and 1037 cm^{-1} for Q^2, 1032 cm^{-1} for Q^3 and 1080 cm^{-1} for Q^4. The bridging oxygen asymmetric stretch is at about 980 cm^{-1} for Q^1-Q^1, and it shifts to about 1100 cm^{-1} with increasing polymerization. This analysis has applications especially for understanding the structure of silica-poor glasses. For instance, two contradicting Raman spectroscopy studies of Mg_2SiO_4 glasses reported the most polymerized SiO_4 tetrahedra in the glass structure to be either Q^0 [1] or Q^3 [2]. Our results indicate that the degree of polymerization is overestimated, if the Si-O-Si stretching modes are not considered in the interpretation of the measured Raman spectra.

[1] Nasikas, N. K. and Chrissanthopoulos, A. and Bouropoulos, N. and Sen, S. and Papatheodorou, G. N., 2011, Chemistry of Materials 23, 3692-3697.
[2] Kalampounias, A. G. and Nasikas, N. K. and Papatheodorou, G. N., 2009, Journal of Chemical Physics 131, 114513.