American Mineralogist, Volume 107, pages 2044–2053, 2022

Effects of electronegativities and charge delocalization on Q^2 Raman shifts of alkaline- and alkaline earth-bearing glasses and metasilicate crystals

H. Wayne Nesbitt[1,*], Phil A.W. Dean[2], G. Michael Bancroft[2], and Grant S. Henderson[3]

[1]Department of Earth Sciences, University of Western Ontario, London, Ontario N6A 5B7, Canada
[2]Department of Chemistry, University of Western Ontario, London, Ontario N6A 5B7, Canada
[3]Department of Earth Science, University of Toronto, Toronto, Ontario M5S 3B1, Canada

Abstract

Raman shifts of the symmetric stretch of silicate Q^2 species vary over a range of ~90 cm^{-1} in crystals and glasses containing alkali and alkaline earth oxides. The shifts display a striking, sympathetic relationship with the electronegativity of the alkali and alkaline earth metals (M), with the highest frequency observed for Mg-silicate glasses and crystals and the lowest frequency for Cs-bearing glasses. Frequencies are determined primarily by the electron density on constituent Si and O atoms of the Q^2 tetrahedra, as measured by Si 2p and O 1s X-ray photoelectron spectra (XPS). The electron density is, in turn, determined by the extent to which electronic charge is transferred from the modifier metal "M" to the NBO of the Q^2 tetrahedron. The charge transferred to NBO is redistributed (delocalized) over all atoms of the tetrahedron by the four equivalent Si sp^3 orbitals. Although negative charge accumulates on all atoms of the tetrahedron, it accumulates preferentially on Si. Coulombic interactions among Si and all O atoms are thus weakened, resulting in decreased force constants and lowered symmetric stretch frequencies of Q^2 species.

Density functional theoretical (DFT) calculations on six staggered and eclipsed $M_6Si_2O_7$ (M = Li, Na, K) molecules corroborate the findings. Charge is transferred from the metal atoms to NBO and delocalized over tetrahedra in accordance with Li, Na, and K electronegativities. Calculated Si-O force constants and Raman shifts decrease with decreasing electronegativity of the cation but surprisingly, calculated Si-NBO bond lengths are largely unaffected, with all being similar at 1.665 ± 0.003 Å.

Keywords: Raman spectroscopy, electronegativity charge delocalization in silicates, tetrahedral symmetric stretch, silicate glasses