

Direct and indirect evidence for free oxygen (O²⁻) in MO-silicate glasses and melts (M = Mg, Ca, Pb)

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ABSTRACT

Oxygen 1s XPS spectra of a Pb-silicate glass containing 76.6 mol% PbO provide the first accurate, direct measurement of free oxide ion (O²⁻) in these glasses. O²⁻ constitutes 35 (±3) mol% of total oxygen, with NBO and BO constituting, respectively, 52 (±3) and 13 (±3) mol%. All ²⁹Si NMR and O 1s XPS results for Pb-silicate glasses indicate mol% levels of O²⁻ containing more than ~30 mol% PbO. The O²⁻ abundances are consistent with equilibrium thermodynamic considerations where $K \sim 12$ for the mass action equation involving NBO, BO, and O²⁻.

Raman and ¹⁷O NMR spectra of two CaMg-silicate glasses indicate ~10 (±4) mol% O²⁻ in CaMgSiO₄ glass and ~18 (±4) mol% O²⁻ in a Ca_{0.36}Mg_{0.36}Si_{0.28}O_{1.28} glass. Oxygen species abundances are calculated using experimental results from 13 separate ²⁹Si NMR, ¹⁷O NMR, and Raman measurements of Mg-, Ca-, and CaMg-silicate glasses. All reveal mol% levels of O²⁻ with ~1 to 2.6 mol% in metasilicate glass and ~5 to 10 mol% in orthosilicate glass. Recent Raman experimental results also indicate O²⁻ in CaMg-silicate glasses at levels ranging from about 1 to 10 mol%. In all there are 23 separate ²⁹Si NMR, ¹⁷O NMR, and Raman measurements indicating mol% levels of O²⁻ in alkaline earth silicate glasses. Eight recent MD simulations of Mg, Ca, and CaMg-silicate glasses include 21 separate simulations over a wide compositional range. All indicate mol% levels of O²⁻ in the glasses demonstrating that the MD simulations and experimental results on these systems are in accord.

There are two fundamentally important implications of these studies. First, free oxygen (O²⁻) is an *essential constituent* of Pb, Mg, Ca, and CaMg binary silicate melts and glasses. It is *not* an “accidental” product associated with glass or melt defects. It is instead, a thermodynamically important constituent of these binary melts (and glasses). Second, where melts are equilibrated, the mass action equation relating BO, NBO, and O²⁻ must hold across the *entire* Ca, Mg, CaMg, and Pb binary systems, thereby requiring the activities and mole fractions of all three species to be defined and finite in the melts. Free oxygen, however, may be too low to be detected in highly siliceous glasses using conventional spectroscopic techniques.

Keywords: XPS of glasses, free oxygen in glasses, silicate glasses, Pb-silicate glass, Ca-silicate glass, Mg-silicate glass, CaMg-silicate glass