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Direct and indirect evidence for free oxygen (O^{2-}) 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 (O^{2-}) in these glasses. O^{2-} constitutes 35 (±3) mol% of total oxygen, with NBO and BO constituting, respectively, 52 (±3) and 13 (±3) mol%. All ^{29}Si NMR and O 1s XPS results for Pb-silicate glasses indicate mol% levels of O^{2-} containing more than ~30 mol% PbO. The O^{2-} abundances are consistent with equilibrium thermodynamic considerations where K ~ 12 for the mass action equation involving NBO, BO, and O^{2-}.

Raman and ^{17}O NMR spectra of two CaMg-silicate glasses indicate ~10 (±4) mol% O^{2-} in $CaMgSiO_4$ glass and ~18 (±4) mol% O^{2-} 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 ^{29}Si NMR, ^{17}O NMR, and Raman measurements of Mg-, Ca-, and CaMg-silicate glasses. All reveal mol% levels of O^{2-} with ~1 to 2.6 mol% in metasilicate glass and ~5 to 10 mol% in orthosilicate glass. Recent Raman experimental results also indicate O^{2-} in CaMg-silicate glasses at levels ranging from about 1 to 10 mol%. In all there are 23 separate ^{29}Si NMR, ^{17}O NMR, and Raman measurements indicating mol% levels of O^{2-} 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 O^{2-} 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 (O^{2-}) 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 O^{2-} 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