The use of cation-cation and anion-anion bonds to augment the bond-valence model

MATTHEW C.F. WANDER[1,*], BARRY R. BICKMORE[1], MATTHEW DAVIS[1], W. JOEL JOHANSEN[1], CHARLES ANDROS[1] AND LARISSA LIND[1]

[1]Department of Geological Sciences, Brigham Young University, Provo, Utah 84602, U.S.A.

ABSTRACT

The bond-valence model has, for several decades, been widely used for creating quantitative structure-activity relationships (QSARs), crystal structure modeling, and verification of proposed structures. Certain limitations of the model, such as the neglect of interactions between cations and between anions, have prevented it from being more broadly applied. In this work, we use cation-cation and anion-anion bonds to augment the existing bonding model in the systems H-Al-Si-O and K-Al-Si-O. The bond valence-length curves for these interactions employ the same mathematical form as ionic bonds, but make only a small contribution to the overall bonding in ionic materials. In the systems examined here, oxygen-oxygen interactions were much more important than those between cations for producing accurate bond-valence sums. Both anion-anion and cation-cation bonding could prove important, however, for our ultimate goal of producing valence-based force fields for use in molecular dynamics simulations. Rolling these interactions into the bond-valence framework would produce behavior similar to hard-sphere repulsive or van der Waals terms, but would more flexibly account for the complete bonding environment. The overall improvement in valence sums was robust, was maintained outside the calibration set, and was invariant to elemental substitution. We conclude that this minor alteration of the bond-valence approach will significantly improve bond-valence models in conjunction with other recent extensions of the approach.

Keywords: Crystal structure, bond valence, ligand, silicate, aluminosilicate