Poster Presentation

MS74.P09

Survey of Bond Lengths in the Solid State for Oxides: Results and Applications

O. Gagne[1], F. Hawthorne[1]

[1]*University of Manitoba, Department of Geological Sciences, Winnipeg, Canada*

A complete survey of bond lengths from the Inorganic Crystal Structure Database (ICSD) is presented for all atoms of the Periodic Table of Elements, bonded to oxygen and in different oxidation states and coordination numbers. From over 135,000 crystal structures, a total of 33,343 coordination polyhedra and 188,462 bond distances were collected after passing a rigorous filtering process. One hundred thirty-six (136) ions in four hundred seventy-three (473) different configurations (coordination numbers) resulted. First, the bondlength distributions are visually inspected. This leads to (1) the observation and visual interpretation of known phenomena (e.g. Jahn-Teller effect), and (2) the isolation of new phenomena, as trends that are less obvious in smaller case-studies become more noticeable. Next, different applications of the data are investigated. The completeness of the survey allows the reassessment of important parameters of the solid state: ionic radii, and bond-valence parameters. Of the 473 ionic radii derived in this study, 329 revisions are made to Shannon's list of radii [1] (of which 176 were estimates), and 144 new ionic radii are derived. Next, a systematic evaluation of all bond-valence parameters published to date is done for oxides. Furthermore, using a new method of derivation, 136 new pairs of bond-valence parameters are obtained. In comparison to the previous-best published bond-valence parameters, an overall average decrease in the r.m.s.d. to the valence-sum rule of 20.7% (12.6% when weighted) is observed for the 33,343 coordination polyhedra, using the new parameters. New equations to describe the bond-length to bond-valence relation are also investigated. From an optimization between the experimental and a priori bond-valences of 54 carefully-selected crystal structures, roughly 20 relatively simple equations were selected for testing. Following a rigorous evaluation, the current exponential equation was found to be a viable choice in describing the relation. Finally, bond-length and bond-valence ranges are assigned to the 473 configurations of the atoms. Whereas the bondlength ranges are a useful aid in structure refinement, the assignment of a bond-valence range to ions allows a priori analysis of site occupancy in crystal structures.

[1] *Shannon, R.D. (1976) Acta Crystallographica, A32, 751–767*

Keywords: Bond-length survey, Bond-valence theory, Ionic radii