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# Zn-O tetrahedral bond length variations in normal spinel oxides

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## Abstract

Six synthetic single crystals of spinel phases with different compositions along the $ZnAl_2O_4$-$ZnCr_2O_4$ solid solution were structurally and chemically characterized by X-ray diffraction and electron microprobe techniques. As predicted, unit-cell parameters and octahedral bond lengths (M-O) increase with increasing replacement of $Al^{3+}$ by $Cr^{3+}$. Despite the constant occupancy of the T site by Zn, also the tetrahedral bond length $^{T}$Zn-O shows significant variations along this binary. These variations are positively correlated with variations in M-O bond lengths.

The present data in conjunction with data from literature provide a basis for quantitative analyses of the variation in $^{T}$Zn-O in normal spinel structures. A negative correlation between $^{T}$Zn-O and the ionic potential at M ($^{M}IP$) suggests that increasing $^{M}IP$ is related to a stronger electrostatic cation-cation repulsion across the shared octahedral edge $^{M}(O\text{-}O)_{shared}$ of the structure. An observed negative correlation between $^{M}IP$ and $^{M}(O\text{-}O)_{shared}$ suggests that a decrease of $^{M}(O\text{-}O)_{shared}$ provides a more efficient shielding effect to reduce the octahedral cation interactions.

In normal $ZnB_2O_4$ spinels (where $B = Al^{3+}$, $Cr^{3+}$, $Ga^{3+}$, $V^{3+}$, $Fe^{3+}$, and $Mn^{3+}$) cations with a smaller size provides a higher charge density. Increasing charge density at the M site causes shortening of $^{M}(O\text{-}O)_{shared}$, which in turn results in shorter $^{T}$Zn-O bond length. In general, variations in $^{T}$Zn-O are required by the structure to better provide an oxygen shielding effect to the octahedral cation-cation repulsion.

**Keywords:** Crystal structure, spinel, XRD data, chemical analysis, $ZnAl_2O_4$, $ZnCr_2O_4$