

Simple Point-Ion Electrostatic Model Explains the Cation Distribution in Spinel Oxides

Vladan Stevanović, Mayeul d'Avezac, and Alex Zunger*

Department of Materials Science and Engineering, University of Colorado, Boulder, Colorado 80401, USA
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The A_2X_4 spinel oxides are distinguished by having either a normal (AB_2X_4) or an inverse (BAB_2X_4) distribution of the A , B cations on their sublattices. A point-ion electrostatic model parametrized by the oxygen displacement parameter δ and by the relative cation valencies ν_A vs ν_B provides a simple rule for the structural preference for normal or inverse: if $\nu_A > \nu_B$ the structure is normal for $\delta > 0.25$ and inverse for $\delta < 0.257$, while if $\nu_A < \nu_B$ the structure is normal for $\delta < 0.2550$ and inverse for $\delta > 0.257$. This rule is illustrated for the known spinel oxides, proving to be $\sim 90\%$ successful.

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The A_2X_4 spinel oxides form a family of ~ 120 compounds [1] spanning a range of physical properties including ferromagnetism [2], coexistence of transparency, and n -type conductivity [3], superconductivity [4], and ferroelectricity [5]. The spinel structure consists of face-centered cubic (fcc) lattice of oxygen anions within which A and B cations occupy octahedral and tetrahedral interstitial sites arranged in one of two possible patterns: normal (AB_2X_4) and inverse (BAB_2X_4). In the normal spinel structure ($Fd\bar{3}m$ space group) the tetrahedral sites are occupied exclusively by the B cations while the octahedral sites are occupied exclusively by A cations. The inverse spinel structure represents a class of configurations in which tetrahedral sites are occupied exclusively by A cations but the octahedral sites can be occupied by both A and B cations possibly in a random fashion. The ~ 120 known oxide spinel compounds are classified experimentally into Normal or Inverse types [1,6]. This includes also dual ($A_2B_2X_4$) spinels which are classified according to their degree of inversion (relative concentration of A on tetrahedral sites) that can be intermediate between normal ($x = 0$) and inverse ($x = 1$). Despite the importance of inversion versus cationic distribution there is still no complete agreement on the nature of the physical and chemical interactions responsible for normal or inverse cationic distributions [1,6–12]. Here we offer a deductive approach based on revisiting the previously discredited [7,13,14

measured values for these should perhaps be revisited experimentally.