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

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The A_2 $_4$ spinel oxides are distinguished by having either a normal ( ) or an inverse ( ) distribution of the A, cations on their sublattices. A point-ion electrostatic model parametrized by the oxygen displacement parameter and by the relative cation valencies $_A$ vs provides a simple rule for the structural preference for or : if $_A >$ the structure is normal for > 0.25 2 and inverse for $<$ 0.257 , while if $_A <$ the structure is normal for < 0.2550 and inverse for > 0.257 . This rule is illustrated for the known spinel oxides, proving to be $\sim$ % successful.

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The A_2 $_4$ spinel oxides form a family of ∼120 compounds [1] spanning a range of physical properties including ferromagnetism [2], coexistence of transparency, and -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 cations occupy octahedral and tetrahedral interstitial sites arranged in one of two possible patterns: - ( ) and ( ). In the normal spinel structure (3 space group) the tetrahedral sites are occupied exclusively by the 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 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 ( ) spinels which are classified according to their degree of inversion (relative concentration of A on tetrahedral sites) that can be intermediate between ($= 0$) and ($= 1$). Despite the importance of versus cationic distribution there is still no complete agreement on the nature of the physical and chemical interactions responsible for or cationic distributions [1,6–12]. Here we offer a deductive approach based on revisiting the previously discredited [7,13,14

3

measured values for these should perhaps be revisited experimentally.