

Effects of cation substitution and order-disorder on *P-V-T* equations of state of cubic spinels

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ABSTRACT

The geometric simplicity of the cubic spinel structure allows prediction of equation-of-state parameters from cation-anion bond distances, bond compressibilities, and bond thermal expansivities, which can be estimated from crystal chemical systematics. We calculate effects of cation substitution and order-disorder reactions for phases of geological interest: MgAl_2O_4 (spinel), MgFe_2O_4 (magnesioferrite), Fe_3O_4 (magnetite), and Mg_2SiO_4 (ringwoodite). Compressibilities for normal vs. inverse variants of $\text{A}^{2+}\text{B}_2^{3+}\text{O}_4$ and $\text{A}^{4+}\text{B}_2^{2+}\text{O}_4$ spinels are predicted to differ by as much as 17%, and thermal expansivities by as much as 15%, as a result of the differential compressibilities or thermal expansivities of divalent, trivalent, and tetravalent cations in tetrahedral vs. octahedral coordination. These effects are unexpectedly large, and they suggest that care must be taken to document the state of cation order before and after any pressure-volume-temperature equation-of-state measurements on phases subject to a range of ordered states.