

Crystal chemistry of the MgAl₂O₄-MgMn₂O₄-MnMn₂O₄ system: Analysis of structural distortion in spinel- and hausmannite-type structures

FERDINANDO BOSI,^{1,2,*} ULF HÅLENIUS,³ AND HENRIK SKOGBY³

¹Dipartimento di Scienze della Terra, Sapienza Università di Roma, P.le A. Moro, 5, I-00185 Rome, Italy

²CNR-IGG Istituto di Geoscienze e Georisorse, Sede di Roma, P.le A. Moro, 5, I-00185 Rome, Italy

³Department of Mineralogy, Swedish Museum of Natural History, Box 50007, 10405 Stockholm, Sweden

ABSTRACT

Single crystals of spinel and hausmannite having seven different compositions in the MgAl₂O₄-MgMn₂O₄-MnMn₂O₄ system were synthesized and structurally and chemically characterized by X-ray diffraction and electron microprobe techniques. As predicted, tetrahedral and octahedral bond lengths increase with increasing substitutions of Mn²⁺ for Mg and Mn³⁺ for Al, respectively. A transition from cubic to tetragonal symmetry occurs at a critical concentration of Mn³⁺ > 1.4 atoms per formula unit as a result of the Jahn-Teller distortion around octahedrally coordinated Mn³⁺.

The present data in conjunction with data from the literature provide a basis for quantitative analyses of the cation polyhedral-distortion parameters and their variations in spinel- and hausmannite-type structures (*Fd $\bar{3}m$* and *I4₁/amd*, respectively). In contrast to the linear correlation between $\langle\lambda_M\rangle$ (octahedral quadratic elongation) and σ_M^2 (octahedral bond-angle variance) observed for many silicates and isomorphous structures, these two distortion parameters are not correlated in multiple oxides with spinel- and hausmannite-type structures. By using a model of multiple linear regression, it is demonstrated that $\langle\lambda_M\rangle$ varies as a function of both σ_M^2 and Δ_M (octahedral bond-length distortion). The degree of octahedral distortion is significant in the spinel structures and is in fact comparable with that calculated for the hausmannite-type structures. The degree of octahedral distortion is related to steric effects in both spinel- and hausmannite-type structures, whereas the electronic effects caused by Mn³⁺ account for the transition from cubic to tetragonal symmetry.

Keywords: Crystal structure, spinel, hausmannite, XRD data, chemical analysis, polyhedral distortion