American Mineralogist, Volume 95, pages 602–607, 2010

Crystal chemistry of the $MgAl_2O_4$-$MgMn_2O_4$-$MnMn_2O_4$ system: Analysis of structural distortion in spinel- and hausmannite-type structures

FERDINANDO BOSI,[1,2,*] ULF HÅLENIUS,[3] AND HENRIK SKOGBY[3]

[1]Dipartimento di Scienze della Terra, Sapienza Università di Roma, P.le A. Moro, 5, I-00185 Rome, Italy
[2]CNR-IGG Istituto di Geoscienze e Georisorse, Sede di Roma, P.le A. Moro, 5, I-00185 Rome, Italy
[3]Department 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 $MgAl_2O_4$-$MgMn_2O_4$-$MnMn_2O_4$ 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 Mn^{2+} for Mg and Mn^{3+} for Al, respectively. A transition from cubic to tetragonal symmetry occurs at a critical concentration of $Mn^{3+} > 1.4$ atoms per formula unit as a result of the Jahn-Teller distortion around octahedrally coordinated Mn^{3+}.

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 $I4_1/amd$, respectively). In contrast to the linear correlation between $\langle\lambda_M\rangle$ (octahedral quadratic elongation) and σ^2_M (octahedral bond-angle variance) observed for many silicates and isomorphic 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^2_M 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 Mn^{3+} account for the transition from cubic to tetragonal symmetry.

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