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

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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 Mn³⁺ 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 Mn⁴⁺.

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 (Fd³m and I₄₁/amd, respectively). In contrast to the linear correlation between <λₜₐₜ> (octahedral quadratic elongation) and σₜₐₜ (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 <λₜₐₜ> varies as a function of both σₜₐₜ and Δₚ (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

INTRODUCTION

Multiple oxides with spinel-type structure may be described by the general formula AB₂O₄, where A and B are usually divalent and trivalent cations, respectively. The symmetry is generally given as space group Fd³m, and the structure can be described as a slightly distorted cubic close packed (CCP) array of anions, in which the A and B cations are distributed in one-eighth of all tetrahedral (T) and half of all octahedral (M) sites. The unit-cell parameters (a, a, a) and oxygen fractional coordinates (x, x, x) define the resulting tetrahedral (T-O) and octahedral (M-O) bond lengths. The distribution of A and B cations over T and M leads to two different ordered configuration schemes: (1) normal spinel, where the A cation occupies T and the two B cations occupy M, and (2) inverse spinel, where one of the B cations occupies T and the remaining A and B cations occupy M. Depending on the nature and electronic configuration of the coordinating cations, the resulting octahedron is distorted (point symmetry 3m), whereas the tetrahedron is always regular (point symmetry 43m). The distortion of the octahedron is a function only of the interbond angles because all the bond lengths are equivalent. The distortion of individual polyhedra and the distortive interactions between the cation-centered polyhedra in spinel-type structures have direct bearing on the stability of these phases in response to composition, temperature, and pressure. Consequently, it is of general importance to arrive at a general (site/polyhedral) distortion concept for spinels and related oxygen-based structures.

The presence of transition element cations with unpaired d-electronic levels causes distortions in both T and M sites, due to the Jahn-Teller effect. In particular, cations with 3d⁴ configuration such as Mn³⁺ in octahedral coordination may produce reduction of the site symmetry from m⁵m to 4/m or lower. In the spinel group minerals this results in two long bond lengths, M-O₄, along the tetragonal axis of the bipyramid, and four shorter ones, M-O₃, in the basal plane. In cubic spinels, when Mn⁴⁺ is present in low concentrations, the bond-length distortion does not produce macroscopic effects, since this distortion occurs at random along the equivalent [100] directions. As soon as a critical Mn³⁺ concentration and critical temperature are reached (Golikov et al. 1989), mutual interactions between second-coordination spheres become important and all octahedra are distorted along the same direction, as in hausmannite (MnMn₂O₄). The general effect is a departure from cubic spinel Fd³m symmetry to tetragonal I₄₁/amd symmetry (Satomi 1961), with the tetragonal c axis approximately parallel to M-O₄ and the four M-O₃ approximately parallel to (001). Consequently, two interbond angles are necessary to describe the distorted octahedron with a 2/m point symmetry. Concomitantly with the octahedral distortion,