Structural relationships in (Mn$_{1-x}$Zn$_x$)Mn$_2$O$_4$ (0 ≤ x ≤ 0.26): The “dragging effect” of the tetrahedron on the octahedron

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ABSTRACT

Ten hausmannite crystals (from Ilfeld and Friedrichrode, Harz, Germany), belonging to the (Mn$_{1-x}$Zn$_x$)Mn$_2$O$_4$ (0 ≤ x ≤ 0.26) system (I4$_1$/amd hausmannite structure type), were characterized by chemical (electron microprobe) and structural (single-crystal X-ray diffractometer) analysis. The prevailing trivalent cation is Mn$^{3+}$, with very minor Al (not higher than 0.005 apfu). Among divalent cations, the main substitution involves Zn → Mn$^{3+}$. Cation distribution was obtained by comparing chemical and structural data, and results confirm normal distribution, with Mn$^{3+}$ ordered on the octahedral site. A specific bond distance of 2.032 Å was refined for $^{3}\text{VIMn}^{3+}$O.

Unit-cell parameters $a$ and $c$ range from 5.752 to 5.763 Å and from 9.408 to 9.461 Å, respectively. The smallest values are characteristic of the sample with the highest hetaerolite content. T-O bond distance (2.027–2.041 Å) shows a strong positive correlation with unit-cell constants, while the O-T-O angle (103.3–103.7°) is related only to the oxygen coordinate, $z$. The two octahedral bond distances show limited variations: the shorter one, M-O$_S$, ranges from 1.927 to 1.930 Å, and is not significantly correlated with unit-cell parameters. The longer one, M-O$_L$, shows a larger variation, from 2.281 to 2.290 Å, and is positively correlated with $c$. Regularization of the octahedron with increasing hetaerolite content coincides with an increase in the oxygen coordinate $y$ and a decrease in $c$ and $c/a$. Of particular interest is the positive linear relation between octahedral elongation and $V_T$. As the octahedral content of all samples is almost constant, given the closeness of Mn$^{3+}$ to stoichiometry, all structural distortions are linked to $^{3}\text{Zn} → ^{3}\text{Mn}^{2+}$ that reduces the T-O bond distance and causes movement of the structure toward cubic symmetry. This interaction is due to the “dragging effect” of the tetrahedron on the octahedron.

In hausmannite-type structures, besides the main structural distortion produced by the Jahn-Teller effect, a secondary one, without symmetry modification, is determined by the geometrical effects of the tetrahedron on the octahedron.

INTRODUCTION

AB$_2$O$_4$ oxides may be described by the $^{3}\text{(A}_1$–$\text{B})^{3}\text{(B}_2$–$\text{A})\text{O}_4$ structural formula, in which IV and VI represent tetrahedrally and octahedrally coordinated sites, A and B are cations with variable valence, and $i$ is the inversion parameter. Depending on the nature and electronic configuration of the coordinating cations, these sites may be more or less distorted. In particular, in the case of the spinel structure (Hafner 1960; Hill et al. 1979), $Fd\bar{3}m$ symmetry results from occupancy of the octahedral (M) and tetrahedral (T) sites, both with fixed coordinates but, whereas the tetrahedron is regular (point symmetry $43m$), the octahedron is distorted (point symmetry $3\text{m}$). However, this distortion only involves the bond angles as all bond distances remain equivalent. The oxygen atom (point symmetry $3\text{m}$) is defined by ($u$, $u$, $u$) coordinates, setting the origin at $3\text{m}$. The cell parameter and oxygen coordinate are therefore functions of tetrahedral and octahedral bond distances (Hill et al. 1979).

Among A and B cations, the presence of transition elements with unpaired external electronic levels causes large distortions in both sites, due to the Jahn-Teller effect. In particular, cations with $3d^0$ or $3d^4$ orbitals such as Cu$^{2+}$ and Mn$^{2+}$, when in octahedral coordination, produce lowering of site symmetry to that of a tetragonal bipyramid, due to the establishment of different interactions along the previously equivalent M-O bonds. In the presence of Mn$^{2+}$, the final results are two long bond distances, M-O$_L$, along the tetragonal axis of the bipyramid, and four shorter ones, M-O$_S$, in the basal plane. In cubic spinels, when $^{3}\text{Mn}^{2+}$ is present in low concentrations, the octahedra are deformed. However, elongation does not produce macroscopic effects such as point symmetry modifications, because the distortions occur at random along the equivalent [100] directions. As soon as a critical $^{3}\text{Mn}^{2+}$ concentration and critical temperature are reached (Golikov et al. 1989), mutual interactions between second-coordination spheres become important and all octahedra are deformed along the same direction, as in hausmannite (MnMn$_2$O$_4$). The general effect is a departure from cubic spinel $Fd\bar{3}m$ symmetry to tetragonal $I4_1/amd$ symmetry (Satomi 1961; Jarosch 1987), with the tetragonal $c$ axis approximately parallel to M-O$_L$ and the four M-O$_S$ approximately