

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

FERDINANDO BOSI,<sup>1,\*</sup> SERGIO LUCCHESI,<sup>1</sup> AND ANTONIO DELLA GIUSTA<sup>2</sup>

<sup>1</sup>Dipartimento di Scienze della Terra, Università di Roma “La Sapienza,” P.le A.Moro 5, 00185 Roma, Italy

<sup>2</sup>Dipartimento di Mineralogia e Petrologia, Università di Padova, C.so G.Garibaldi 37, 35122 Padova, Italy

### ABSTRACT

Ten hausmannite crystals (from Ilfeld and Friedrichrode, Harz, Germany), belonging to the  $(\text{Mn}_{1-x}\text{Zn}_x)\text{Mn}_2\text{O}_4$  ( $0 \leq x \leq 0.26$ ) system (*I4<sub>1</sub>/amd* hausmannite structure type), were characterized by chemical (electron microprobe) and structural (single-crystal X-ray diffractometer) analysis. The prevailing trivalent cation is  $\text{Mn}^{3+}$ , with very minor Al (not higher than 0.005 apfu). Among divalent cations, the main substitution involves  $\text{Zn} \rightarrow \text{Mn}^{2+}$ . Cation distribution was obtained by comparing chemical and structural data, and results confirm normal distribution, with  $\text{Mn}^{3+}$  ordered on the octahedral site. A specific bond distance of 2.030 Å was refined for  $^{55}\text{Mn}^{3+}\text{-O}$ .

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,  $\text{M-O}_s$ , ranges from 1.927 to 1.930 Å, and is not significantly correlated with unit-cell parameters. The longer one,  $\text{M-O}_L$ , 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  $\text{Mn}^{3+}$  to stoichiometry, all structural distortions are linked to  $^{IV}\text{Zn} \rightarrow ^{IV}\text{Mn}^{2+}$  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.