

Tetrahedral vacancies and cation ordering in low-temperature Mn-bearing vesuvianites: Indication of a hydrogarnet-like substitution

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ABSTRACT

Strongly zoned Mn-rich vesuvianites with MnO concentrations up to 14.3 wt% from the N'chwaning II mine of the Kalahari manganese field (South Africa) crystallized at hydrothermal conditions below 450 °C. These vesuvianites are by far the most Mn-rich samples hitherto described and have either space group *P4nc* or *P4/n* due to partial long-range ordering. Most crystals are assembled of *P4nc* and *P4/n* domains yielding *P4* average symmetry. The crystal structure of one Mn-rich crystal of average composition $\text{Ca}_{19}\text{Mn}_{3.5}\text{Al}_{9.5}\text{Si}_{17.4}(\text{O},\text{OH})_{78}$ was refined from single-crystal X-ray data ($R1 = 3.85\%$) in space group *P4/n* ($a = 15.571(2)$, $c = 11.789(2)$ Å). Mn^{2+} and Mn^{3+} are concentrated on the fivefold-coordinated square pyramidal Y' site. Additional Mn^{3+} was located on the octahedral sites Y2a (35%), Y1a (22%), Y2b (13%) and Y1b (8%). Electron microprobe analyses and crystal-structure refinements indicated tetrahedral vacancies in the orthosilicate tetrahedra (Z1 and Z2) but not in the disilicate units (Z3). Z1 tetrahedra with up to 17% vacancies have strongly increased Z1-O distances of 1.67 Å. Structural and chemical evidence combined with the similarity of the structures of vesuvianite and garnet suggest a partial hydrogarnet-like substitution of SiO_4 tetrahedra by H_4O_4 .