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Crystal chemistry of layered Pb oxychloride minerals with PbO-related structures: Part II. Crystal structure of vladkrivovichevite, $[Pb_{32}O_{18}][Pb_4Mn_2O]Cl_{14}(BO_3)_8 \cdot 2H_2O$

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Abstract

The crystal structure of vladkrivovichevite, a new complex lead oxychloride mineral from the Kombat Mine, Grootfontein, Namibia, has been solved by direct methods and refined to $R_1 = 0.048$ for 3801 unique observed reflections. The mineral is orthorhombic, *Pmmn*, $a = 12.759(1)$, $b = 27.169(4)$, $c = 11.515(1)$ Å, and $V = 3992.0(9)$ Å^3. The structure of vladkrivovichevite belongs to a novel type of layered Pb oxychloride structure. The structure contains 12 symmetrically independent Pb sites. All Pb sites have strongly asymmetric coordination. Two B atoms form slightly distorted BO_3 triangles. One symmetrically independent Mn atom forms five Mn-O bonds and one Mn-Cl bond by forming MnO_5Cl octahedra. The O1, O2, O10, O11, and O12 atoms are tetrahedrally coordinated by four Pb atoms each, forming OPb_4 oxocentered tetrahedra. The O7 site has a remarkable octahedral coordination, consisting of four Pb and two Mn atoms. The $O1Pb_4$, $O2Pb_4$, $O10Pb_4$, and $O11Pb_4$ tetrahedra share common edges to produce bands interconnected by $O12Pb_4$ tetrahedra, forming a $[O_{18}Pb_{32}]^{28+}$ layer. A $O7Pb_4Mn_2$ heterometallic oxocentered octahedron serves as the core of the $[OPb_4Mn_2Cl_2(BO_3)_8]^{16-}$ clusters that link to the $[O_{18}Pb_{32}]^{28+}$ layer via BO_3 triangles. The presence of $[OPb_4Mn_2Cl_2(BO_3)_8]^{16-}$ clusters is associated with large cross-like vacancies in the $[O_{18}Pb_{32}]^{28+}$ layer.

Keywords: Vladkrivovichevite, lead oxyhalides, crystal structure, litharge derivatives, layered structures, oxocentered units, borates, complex topologies