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Crystal chemistry of layered Pb oxychloride minerals with PbO-related structures: Part I. Crystal structure of hereroite, $[Pb_{32}O_{20}(O,\square)](AsO_4)_2[(Si,As,V,Mo)O_4]_2Cl_{10}$

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Abstract

The crystal structure of hereroite, a new complex lead oxychloride mineral from the Kombat Mine, Grootfontein, Namibia, has been solved by direct methods and refined to $R_1 = 0.054$ for 6931 unique observed reflections. The mineral is monoclinic $C2/c$, $a = 23.139(4)$, $b = 22.684(4)$, $c = 12.389(2)$ Å, $\beta = 102.090(3)°$, and $V = 6358.8(18)$ Å^3. The structure contains 16 independent Pb sites in strongly asymmetric coordination by O and Cl atoms. There are two tetrahedral sites, from which one (As) is occupied solely by As, whereas the second (T) has the mixed occupancy of $[Si_{0.48}As_{0.29}V_{0.15}Mo_{0.09}]$. There are in total 21 O sites. The O1–O8 sites belong to the AsO_4 and TO_4 tetrahedral oxyanions. The other O atoms (O9–O20) are tetrahedrally coordinated by Pb atoms, thus being central for the OPb_4 oxocentered tetrahedra. The OPb_4 tetrahedra share edges to form the $[O_{21}Pb_{32}]^{22+}$ layers that can be described as derivatives of the [OPb] layer from the structure of tetragonal PbO (litharge). The $[O_{21}Pb_{32}]^{22+}$ layer in hereroite can be obtained from the [OPb] layer by removal of blocks of oxocentered tetrahedra, which results in formation of double-square sevenfold and square fourfold cavities. The cavities are occupied by the AsO_4 and TO_4 tetrahedra, respectively. The topology of the $[O_{21}Pb_{32}]^{22+}$ layer is complex and can be described as a combination of modules extracted from the layers of OPb_4 tetrahedra present in the structures of kombatite and symesite. The topological functions of tetrahedra within the layer are analyzed using the square lattice method, which shows that each symmetry-independent tetrahedron has its own topological function in the layer construction. The structure of hereroite belongs to the 2:1 type of layered Pb oxyhalides and consists of alternating PbO-type layers and Cl sheets oriented parallel to the (010) plane.

Keywords: Hereroite, lead oxyhalides, crystal structure, litharge derivatives, layered structures, oxocentered tetrahedra, modular structures, method of square lattices