

m20.p12

Pb₃₁O₂₂Br₁₀Cl₈ - the new lead-oxihalide compound with the most complex tetrahedral structure

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Keywords: oxyhalides, crystal structure, oxocentered tetrahedra

Lead oxyhalides represent an important class of inorganic materials with possible applications as ionic conductors and highly anisotropic nanomaterials. We report herein the synthesis and structure of Pb₃₁O₂₂Br₁₀Cl₈ (**1**), a high-temperature phase in the PbO-PbCl₂-PbBr₂ system that has been obtained by rapid quenching of Pb oxyhalide melt. The structure of **1** (triclinic, P $\bar{1}$, $a=12.1192(7)\text{\AA}$, $b=16.2489(10)\text{\AA}$, $c=18.3007(11)\text{\AA}$, $\alpha=93.104(2)^\circ$, $\beta=95.809(2)^\circ$, $\gamma=111.252(1)^\circ$, $V=3325.4(3)\text{\AA}^3$, $Z=2$) is remarkable in many ways. It contains 31 symmetrically independent Pb²⁺ cations, 18 halide sites statistically occupied by Br⁻ and Cl⁻ ions, and 22 oxygen positions. The Pb²⁺ cations of the Pb(1) to Pb(30) sites have mixed oxyhalide coordination with $m\text{O} + n\text{X}$ anions ($\text{X} = \text{Br}, \text{Cl}$). The structure of **1** can be described as incorporation of [PbX₆]⁴⁻ halide units into a defect PbO oxide matrix. The latter represents a 2-dimensional (2D) [O₂₂Pb₃₀]¹⁶⁺ cationic layer of the OPb₄ tetrahedra (Fig. 1).

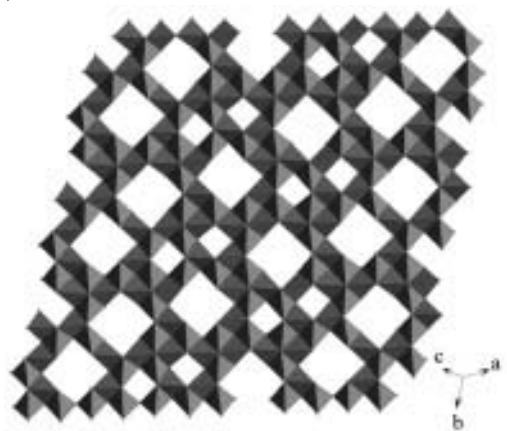


Fig. 1 The [O₂₂Pb₃₀]¹⁶⁺ 2D layer composed from edge-sharing OPb₄ tetrahedra

In the structure of **1**, holes in the 2D PbO matrix correspond to either single tetrahedra or 2x2-blocks. The Pb oxide [O₂₂Pb₃₀]¹⁶⁺ block in the structure of **1** is remarkable in its exceptional topological complexity which has no analogs among the known PbO derivatives [1]. It consists of 22 symmetrically independent OPb₄ tetrahedra that, in addition, play different roles in the topological organization of the layer. So, this PbO-related arrangement represents the topologically most complex tetrahedral structure known so far.

[1] Krivovichev, S. V.; Armbruster, T.; Depmeier, W. J. *Solid State Chem.* 2004, 177, 1321-1332.

m20.p13

Crystal structures and topology of two modifications of holtite

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Keywords: topology, mineral crystal structures, X-ray diffraction

The crystal structures of two modifications of the mineral holtite (holtite I and II) from the Kola Peninsula (Russia) are presented. The most specific feature of the crystal structures of both modifications of holtite is an octahedral framework formed by two types of nonequivalent columns of Al octahedra. This framework was found previously in the structures of dumortierite [1] and magnesiodumortierite [2]. In one type of columns, pairs of equivalent Al-octahedra share faces, whereas nonequivalent Al-octahedra in the other type of columns are linked to each other by edges. In both holtite I and holtite II structures triangular BO₃ anions occupy relatively narrow channels of triangular cross section, parallel to the [100] direction. The differences in the structures of holtite II and holtite I are associated with different composition and configuration of the columns of Al,Ta-polyhedra, which are located in wide channels of hexagonal cross section and are linked to Si-tetrahedra, as well as with the arrangement of pyramidal Sb,As-groups which statistically substitute Si-tetrahedra.

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[2] Ferraris G., Ivaldi G., Chopin C. *Eur. J. Mineral.*, 1995, 7, 167.