Pb oxyhalides are of interest due to their environmental and technological importance. They are also known as important constituents of oxidation zones of mineral deposits. Most Pb oxyhalides have layered α-PbO-derivative structures, which are related to the Aurivillius phases. The crystal structures of Pb-O related layered lead oxyhalides are based upon the O−Pb layers alternating with the X sheets of X− ions (X = Cl, Br, I). The PbO-derivative compounds may also incorporate a wide range of elements, including As, S, V, Mo, W, P, Si, etc., which results in interesting chemical and structural diversity and complexity. Pb₃[Pb₂₀O₁₀](GeO₄)Cl₁₀ (1) was obtained by rapid quenching of lead-oxyhalide melt [1]. The structure of 1 (Cmca, a = 28.352(19), b = 11.116(7), c = 16.513(11) Å, V = 5204(6) Å³, R1 = 0.0504) contains 7 symmetrically independent Pb sites. Pb(6) site is splitted into less occupied Pb6A and Pb6B sites. The coordination environments of the Pb atoms are variable in agreement with the presence of stereochemically active "lone pairs" on divalent lead cations. The structure of 1 contains one Ge site coordinated tetrahedrally by four O atoms with the average <Ge-O> bond length equal to 1.75 Å. The total number of oxygen sites is seven. The O(3), O(4), O(6), and O(7) sites are bonded to Ge, whereas other O atoms (O(1), O(2), O(5)) are tetrahedrally coordinated by Pb atoms, which results in formation of oxocentered OPb₄ tetrahedra. 1 belongs to the 1:1 type and consists of alternating PbO-type layers and mixed Pb−Cl sheets oriented parallel to (100). The PbO-type layer is a derivative of the [OPb] tetrahedral layer in α-PbO and can be obtained from the latter by removal of blocks of oxocentered tetrahedra. The GeO₄ tetrahedral anions locate in the cavities within the PbO-type layer. The formula of the layer can be written as [O₁₀Pb₂₀]²⁻. The structure of 1 illustrates the complexity of the lead oxyhalide systems and validates new pathways for synthesis of complex Pb oxyhalides.


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