

## **Structural complexity of lead silicates: Crystal structure of $\text{Pb}_{21}[\text{Si}_7\text{O}_{22}]_2[\text{Si}_4\text{O}_{13}]$ and its comparison to hyttsjöite**

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### **ABSTRACT**

The crystal structure of  $\text{Pb}_{21}[\text{Si}_7\text{O}_{22}]_2[\text{Si}_4\text{O}_{13}]$  has been solved on crystals grown by crystallization from melt. The compound is hexagonal,  $P6_3/m$ ,  $a = 9.9244(5)$ ,  $c = 34.2357(16)$  Å,  $V = 795.28(6)$  Å<sup>3</sup>,  $R_1 = 0.042$  for 3361 unique observed reflections. The structure contains five symmetrically independent Si sites tetrahedrally coordinated by O atoms. The  $\text{Si1O}_4$ ,  $\text{Si3O}_4$ , and  $\text{Si4O}_4$  tetrahedra share corners to form branched heptameric  $[\text{Si}_7\text{O}_{22}]^{16-}$  units, whereas the  $\text{Si2O}_4$  and  $\text{Si5O}_4$  tetrahedra form the tetrameric  $[\text{Si}_4\text{O}_{13}]^{10-}$  anions. The structure contains six symmetrically independent Pb sites with the  $\text{PbO}_n$  coordination polyhedra distorted due to the stereochemical activity of the lone electron pairs. The structure can be described as a stacking of layers of the two types, A and B. The A-type layer contains  $[\text{Si}_7\text{O}_{22}]^{16-}$  units, Pb1, Pb2, Pb3, and Pb4 sites, whereas the B-type layer contains  $[\text{Si}_4\text{O}_{13}]^{10-}$  anions, together with Pb5, Pb6, and Pb6A sites. Stacking of the layers can be described as a sequence ...AA'BAA'B..., where A and A' denote A layers with opposite orientations of the tripod-shaped silicate heptamers. The crystal structure of  $\text{Pb}_{21}[\text{Si}_7\text{O}_{22}]_2[\text{Si}_4\text{O}_{13}]$  has many similarities to that of hyttsjöite, which contains the same layers consisting of tripod-shaped  $[\text{Si}_7\text{O}_{22}]^{16-}$  anions. In both title compound and hyttsjöite, the anions are stacked together in such a way that ellipsoidal cavities with dimensions of ca.  $10 \times 6 \times 6$  Å<sup>3</sup> are created. The cavities are occupied by the  $\text{ClPb}_6$  octahedra in hyttsjöite and by “empty”  $\text{Pb}_6$  octahedra in  $\text{Pb}_{21}[\text{Si}_7\text{O}_{22}]_2[\text{Si}_4\text{O}_{13}]$ . Analysis of structural and chemical complexity in the  $\text{PbO-SiO}_2$  system indicates that the most chemically complex phases (in terms of complexity of relations between chemical components) appear to be the most complex from the structural point of view as well. The title phase is the most structurally and chemically complex phase in the system. Structural organization of crystalline phases in the  $\text{PbO-SiO}_2$  system can be described as controlled by the Pb:Si ratio. For the phases with Pb:Si <2, their structures contain  $\text{Pb}^{2+}$  ions and silicate anions. For the phases with Pb:Si <2, the structures contain “additional” O atoms, i.e., atoms that are not bonded to Si. These atoms form  $\text{OPb}_4$  tetrahedra, which are the next strongest structural subunits in the structure after silicate anions. The structures of the phases with Pb:Si <2 can therefore be described as based upon silicate anions and polynuclear cationic units consisting of edge- and corner-sharing  $\text{OPb}_4$  tetrahedra.

**Keywords:** Lead silicate; new mineral; crystal structure; hyttsjöite; lone electron pair stereoactivity; structural complexity