

m41.p29**Crystal chemistry of divalent lead:
Characteristics of Pb-Ox-Cl-polyhedra**

Franz Pertlik

*Institut für Mineralogie und Kristallographie, Geozentrum, Universität Wien, Austria. E-mail: franz.pertlik@univie.ac.at***Keywords: crystal chemistry, coordination, lead compounds**

Size and shape of a coordination polyhedron built up by its appertaining atoms (in the special case a central lead atom coordinated by oxygen and chlorine atoms) is defined by its space filling polyhedron based in an arbitrary manner on the ratio of the radii with $\text{Pb}:\text{O}:\text{Cl}=1:1:1$. As a consequence, the faces of each polyhedron cut the distance between central atom and coordinating atom in half [1].

Rather typical for formally divalent lead is the frequent occurrence of one-sided coordination polyhedra. Crystal chemical calculations concerning the coordination polyhedra of divalent lead, in which both the two elements oxygen and chlorine are involved, show two interesting features. The two features in the geometric arrangement are: (1) The irregularity of the coordination polyhedra, which can be deduced from the configuration of the electrons, especially of the lone pair 6s electrons of divalent lead. (2) A tendency of O and Cl atoms to be arranged in different hemispheres around the central lead atom [2].

The following values are further results of statistic investigations of the distances: In Pb-O-polyhedra the mean $\langle \text{Pb}-\text{O} \rangle$ distance measures 2.5 Å, in Pb-Cl-polyhedra $\langle \text{Pb}-\text{Cl} \rangle > 2.9$ Å. If both ligands participate, the distances are $\langle \text{Pb}-\text{O} \rangle \approx 2.4$ Å and $\langle \text{Pb}-\text{Cl} \rangle \approx 3.2$ Å. These calculations and statistic investigations confirm the more or less sophisticated bond valences determined from bond lengths.

[1] Nowotny, H., Zobetz, E., Unpublished computer program. 1982.

[2] Pertlik, F., Z. Kristallogr., 1988, 184, 191.

m41.p30**Synthesis and crystal Structures of high temperature borate in REE_2O_3 - Al_2O_3 - CuO - B_2O_3 system**

Paul Plachinda, Elena Belokoneva

*Department of Materials Science and Department of Geology, Lomonosov State University, Leninskie Gori, GSP-2, Moscow 119899, Russia E-mail: plachinda@inorg.chem.msu.ru***Keywords: crystallization of materials, high-temperature compounds, X-ray crystal structure determination**

Crystal chemistry of mixed boron - aluminum oxides is of interest due to the possibility of formation two different classes of compounds - borates of aluminum and alumoborates, where Al being coordinated either octahedral or tetrahedral, together with boron in tetrahedral or triangle coordination, could form various structures. Application interest to these compounds comes from the possibility to use it as optical materials. Synthetic borate analogues of Ca,Mg carbonate huntite, $\text{REE}(\text{Al},\text{Sc},\text{Fe})_3(\text{BO}_3)_4$ are known as promising crystals for laser generation with self frequency doubling. Adding of Cu in this system could lead to crystallization of compounds with unusual crystal structures.

We have studied the products of annealing at 1000C -1100C mixtures from the following sets: 1) REEB_3O_6 - CuB_2O_4 - Al_2O_3 , (REE= La, Nd, Pr, Eu, Sm) 2) REEBO_3 - CuB_2O_4 - Al_2O_3 (REE=Tb, Dy, Ho, Er, Tm, Yb, Y).

Single crystals of known compounds $\text{LaAl}_{2.03}(\text{B}_4\text{O}_{10})\text{O}_{0.54}$ [1] and $\text{CuTb}_2(\text{B}_8\text{O}_{16})$ [2] have been obtained. Pr, Eu, Tb Aluminum borate form different polytypes of the huntite structural family known for Nd and Gd [3]:

Compound	S.G.	a,Å	b,Å	c,Å	β ,°
$\text{PrAl}_3(\text{BO}_3)_4$	C2/c	7.272(2)	9.351(5)	11.148(2)	103.55(2)
$\text{EuAl}_3(\text{BO}_3)_4$	C2	7.231(1)	9.326(4)	16.216(4)	90.71(2)
$\text{TbAl}_3(\text{BO}_3)_4$	C2/c	7.220(3)	9.312(4)	11.072(4)	103.20(3)

The compound $\text{Al}_6\text{Cu}_2\text{B}_4\text{O}_{17}$, previously solved on powder [4] has been obtained as a single crystals and its structure has been refined ($a=10.577(6)$, $c=5.679(1)$, sp.gr. I4/m). Lu-run led to form crystals of a new structural type. Single crystal X-Ray experiment gave $a=12.611(4)$, $c=4.727(4)$, sp.gr P-4m2. Preliminary results show the following stoichiometry: $\text{Lu}_8\text{Cu}_{1/2}\text{Al}_{1/3}\text{B}_{16}\text{O}_{37}$. The peculiarity of this structure is a formation of building block, previously selected in borophosphates - 5 tetrahedrons "airscrew" (BP_4O_{16}). However, in Lu-compound, $(\text{Cu},\text{Al})\text{O}_4$ plays the role of central tetrahedron instead of BO_4 . Cross-linked by BO_3 triangles, these "airscrews" form layers. The structure has zeolitic character with 2 different types of channels with section of 3.2Å, occupied by Lu, and other with section of 6.5Å.

The authors acknowledge financial support from Russian Foundation for Basic Researches under Grants No. 05-03-32719-a and 05-03-32154-a.

[1] Yang, P.; Yu, W.; Wang, J.-Y.; Wei, J.Q.; Liu, Y.G. Acta Cryst. (1998), C54, 11-12.

[2] Schaefer, J.; Bluhm, K. Zeitschr. fuer Naturforsch. B. Anorg. Chem., Org. Chem. (1995), 50, 757-761.

[3] Belokoneva, E.L.; Timchenko, T.I. Kristallografiya, (1983), 28, 1118-1123.

[4] Kaduk, J.A.; Satek, L.C.; McKenna, S.T. The Rigaku Journal (1999), 16(2), 17-30.