

Refinement of the Structure of Lead Hexaaluminate ($\text{PbAl}_{12}\text{O}_{19}$)

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Hexaaluminates are known to have a β -alumina, magnetoplumbite, or related layer structure. These structures consist of "spinel blocks" and "conduction layers," which are stacked alternately. Spinel blocks are composed only of Al^{3+} and O^{2-} ions, having the same rigid structure as spinel. Large cations such as Na^+ , K^+ , Sr^{2+} , and La^{3+} are usually accommodated in the spacious conduction layer which has a mirror symmetry plane. The major differences between β -alumina and magnetoplumbite exist in the contents and arrangement of the ions within the conduction layer (for details see Ref. (1).) The hexagonal aluminates containing small divalent cations such as Ca^{2+} and Sr^{2+} were revealed to have magnetoplumbite structure with a formula $M\text{Al}_{12}\text{O}_{19}$, where $M = \text{Ca}$, Sr , by the single crystal X-ray structure analysis (2-4). On the other hand, the hexaaluminate having a large divalent ion, Ba^{2+} , has been studied for the last decade by many researchers and is now known to have a β -alumina structure (5, 6). As for the element of intermediate ionic size, Pb^{2+} , X-ray powder and electron diffraction data (7), which suggested magnetoplumbite structure, were published, but the structure parameters were not yet determined.

This note reports the structure parameters of Pb hexaaluminate obtained by the single crystal X-ray diffraction method.

The single crystals were grown by the slow cooling method (8). $\text{PbO}-\gamma\text{Al}_2\text{O}_3$ mixture (9:1 in weight) was molten and kept at 1300°C for 2 days and then cooled down slowly to room temperature. Small Pb hexaaluminate single crystals were produced together with Al_2O_3 crystals. The obtained crystals were very brittle. Among them, some specimens having good shape were selected and the crystallinity was checked by the X-ray precession photographs. The X-ray photos also revealed that the structure belonged to the hexagonal space group $P6_3/mmc$ and showed no sign of superstructure. Using a $0.16 \times 0.16 \times 0.06$ -mm rectangular crystal, intensity data were collected on an automatic four-circle diffractometer (AFC-3, Rigaku Denki Co.) using graphite monochromatized $\text{MoK}\alpha$ radiation. The final set of 546 nonzero independent reflections below $2\theta = 120^\circ$ was corrected for Lorenz polarization and absorption effects. The lattice parameters were determined to be $a = 5.5711(3)$ Å and $c = 22.045(2)$ Å on the basis of 2θ -data collected on the four-circle diffractometer. Since the linear absorption coefficient was

TABLE I
 THE POSITIONAL^a AND THERMAL PARAMETERS^b

	Position	Number per unit cell	x	z	$\beta_{11} \times 10^4$	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^5$	$\beta_{23} \times 10^5$
Pb	2d	2	$\frac{2}{3}$	$\frac{1}{4}$	112(2)	β_{11}	75(2)	0
Al(1)	12k	12	0.8317(4)	0.1080(1)	33(5)	30(7)	21(3)	6(21)
Al(2)	4f	4	$\frac{1}{3}$	0.02809(18)	30(8)	β_{11}	13(5)	0
Al(3)	4f	4	$\frac{2}{3}$	0.19013(18)	34(8)	β_{11}	21(5)	0
Al(4)	2a	2	0	0	21(13)	β_{11}	30(9)	0
Al(5)	4e	2	0	0.2406(5)	31(17)	β_{11}	96(31)	0
O(1)	12k	12	0.1545(7)	0.0519(2)	45(12)	34(22)	15(5)	-7(30)
O(2)	12k	12	0.5016(7)	0.1471(2)	41(13)	57(19)	12(6)	11(34)
O(3)	4f	4	$\frac{2}{3}$	0.0541(4)	19(16)	β_{11}	34(12)	0
O(4)	4e	4	0	0.1479(4)	14(18)	β_{11}	36(14)	0
O(5)	6h	6	0.1823(11)	$\frac{1}{4}$	50(21)	98(41)	42(10)	0

^a $y = 2x$.

^b The thermal parameters are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. $\beta_{12} = \frac{1}{2}\beta_{22}$; $\beta_{13} = \frac{1}{2}\beta_{23}$.

 TABLE II
 INTERATOMIC DISTANCES

	Number of bonds	Distance (Å)
Octahedral coordination		
Al(1)-O(1)	2	1.992(7)
-O(2)	2	1.811(7)
-O(3)	1	1.987(6)
-O(4)	1	1.847(6)
Al(3)-O(2)	3	1.880(7)
-O(5)	3	1.966(8)
Al(4)-O(1)	6	1.879(6)
Tetrahedral coordination		
Al(2)-O(1)	3	1.804(7)
-O(3)	1	1.812(10)
Polyhedron 5-coordinated		
Al(5)-O(4)	1	2.044(14)
-O(4)'	1	2.458(14)
-O(5)	3	1.771(11)
Polyhedron 12-coordinated		
Pb -O(2)	6	2.772(5)
-O(5)	6	2.790(9)

as large as $\mu = 156 \text{ cm}^{-1}$, absorption correction due to crystal shape was applied. Absorption correction was based on the algorithm of Busing and Levy (9). The neutral scattering factors were taken from Ref. (10). The full matrix least-squares program was a modified version of RSFLS-4 (11) and Fourier syntheses were done by using RSSFR-5 (12).

As the starting parameters, those of Sr hexaaluminate (4) were used. The refinement converged quickly, and the final anisotropic refinement gave a final R value of 0.043 ($wR = 0.054$, $w = 1.0$). The difference Fourier synthesis at this stage showed peaks and depressions in the range of -2 to $8 \text{ e}\text{\AA}^{-3}$, with the minimum at (0.80, 0.48, 0.25) and the maximum at (0.66, 0.33, 0.22). The final parameters are given in Table I, and the bond lengths and angles are presented in Tables II and III, respectively.

The obtained parameters correspond to a structure of magnetoplumbite type. The shift of Al (5) from the ideal 2b site (0, 0,

TABLE III
 BOND ANGLES^a

	Bond angle (°)
Octahedral coordination	
O(1)–Al(1)–O(1)'	80.80(37)
–O(2)	89.75(29)
–O(3)	88.98(26)
–O(4)	84.71(24)
O(2)–Al(1)–O(3)	86.12(21)
–O(4)	99.20(25)
O(2)–Al(3)–O(2)'	96.79(25)
–O(5)	91.07(33)
O(5)–Al(3)–O(5)'	79.87(34)
O(1)–Al(4)–O(1)'	86.79(24)
–O(1)''	93.21(24)
Tetrahedral coordination	
O(1)–Al(2)–O(1)'	111.90(17)
–O(3)	106.92(19)
Polyhedron 5-coordinated	
O(5)–Al(5)–O(4)	96.72(36)
–O(4)'	83.28(36)
–O(5)'	118.65(14)

^a Primes (' , '') indicate the symmetrically equivalent atoms at different positions.

0.25) to the 4e site has been reported in the magnetoplumbite structure (2, 3) and was also observed in the present compound. It had a stoichiometric composition with a chemical formula of PbAl_2O_9 ($Z = 2$). No defect structure was observed. The contents of Pb and Al were revealed to be 26.6 and 38.7 wt%, respectively, by electron mi-

croprobe analysis (Theoretical values are 24.8 wt% for Pb and 38.8 wt% for Al.) Hexaaluminates take β -alumina structure if the cation on the mirror plane has large ionic size. The present result shows that a β -alumina-magnetoplumbite structure field boundary lies between Ba^{2+} and Pb^{2+} ions in the case of divalent cations.

References

1. N. IYI, S. TAKEKAWA, AND S. KIMURA, *J. Solid State Chem.* **83**, 8 (1989).
2. K. KATO AND H. SAALFELD, *N. Jb. Miner. Abh.* **109**, 192 (1968).
3. A. UTSUNOMIYA, K. TANAKA, H. MORIKAWA, F. MARUMO, AND H. KOJIMA, *J. Solid State Chem.* **75**, 197 (1988).
4. A. J. LINDOP, C. MATTHEWS, AND D. W. GOODWIN, *Acta Crystallogr. Sect. B* **31**, 2940 (1975).
5. N. IYI, Z. INOUE, S. TAKEKAWA, AND S. KIMURA, *J. Solid State Chem.* **52**, 66 (1984).
6. F. P. F. VAN BERKEL, H. W. ZANDBERGEN, G. C. VERSHOOR, AND D. J. W. IDO, *Acta Crystallogr. Sect. C* **40**, 1124 (1984).
7. J. J. COMER, W. J. CROFT, M. KESTIGIAN, AND J. R. CARTER, *Mater. Res. Bull.* **2**, 293 (1967).
8. S. TAKEKAWA, unpublished data (1984).
9. W. R. BUSING AND H. A. LEVY, *Acta Crystallogr.* **10**, 180 (1957).
10. J. A. IBERS AND W. C. HAMILTON, "International Tables for X-ray Crystallography," Vol 4, Kynich, Birmingham (1974).
11. T. SAKURAI, K. NAKATSU, H. IWASAKI, AND M. FUKUHARA, RSFLS-4, UNICS II, the Crystallographic Society of Japan (1967).
12. T. SAKURAI, RSSFR-5, UNICS II, the Crystallographic Society of Japan (1967).