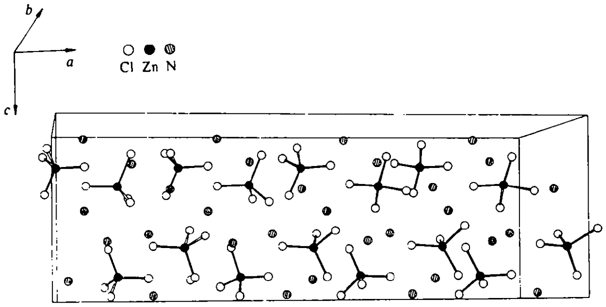

Fig. 1. Arrangement of the atoms viewed along the *b* axis.

eightfold coordination. With the Zn—Cl tetrahedra the 5 and 7 polyhedra share one face, one vertex and two edges and the 6 and 8 polyhedra share two vertices and two edges.

The main structural differences between the K^+ and NH_4^+ compounds lie in the details of the coordination about the cation. Even though the differences in the details of coordination mean that $(NH_4)_2[ZnCl_4]$ cannot be considered strictly isostructural with $K_2[ZnCl_4]$ and its isotypes, the similarities in coordination and in the basic arrangement of the structural elements are greater than those necessarily implied by the term 'isopuntal'.

We would like to thank Dr K. Peters and Mrs E. Peters for their valuable help.

This work was supported by the Deutsche Forschungsgemeinschaft.

References

Follner, H. & Brehler, B. (1970). *Acta Cryst.* B**26**, 1679–1682.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

Jacobi, H. (1969). *Naturwissenschaften*, **56**, 368.

Jacobi, H. (1970). *Z. Kristallogr.* **129**, 434–435.

Jacobi, H. & Brehler, B. (1969). *Z. Kristallogr.* **128**, 390–405.

Mikhail, I. & Peters, K. (1979). *Acta Cryst.* B**35**, 1200–1201.

Vermin, W. J., Verschoor, G. C. & IJdo, D. J. W. (1976). *Acta Cryst.* B**32**, 3325–3328.

Acta Cryst. (1980). B**36**, 2128–2130

Structure of a Lead Apatite $Pb_9(PO_4)_6$

By Mayumi Hata, Fumiyuki Marumo and Shin-ichi Iwai

Research Laboratory of Engineering Materials, Tokyo Institute of Technology, Nagatsuta 4259, *Midori-ku, Yokohama, Japan*

and Hideki Aoki

Division of Inorganic Materials, Institute for Medical and Dental Engineering, Tokyo Medical and Dental University, Chiyoda-ku, Tokyo 101, *Japan*

(*Received* 31 *January* 1980; *accepted* 18 *April* 1980)

Abstract. $Pb_9(PO_4)_6$, hexagonal, $P6_3/m$, $a = 9{\cdot}826$ (4), $c = 7{\cdot}357$ (3) Å, $Z = 1$. Crystals were grown from the melt of a product prepared by a hydrothermal reaction of $Pb(CH_3COO)_2.3H_2O$ and K_2HPO_4 at 473 K. Structure refinement was carried out by the full-matrix least-squares method to $R = 0{\cdot}043$ with 490 independent X-ray reflection data. This crystal is of an apatite structure type and is deficient in Pb at the Pb(1) site, with the OH group missing.

Introduction. Several reports exist on compounds of the lead apatite group. Bhatnagar (1971) synthesized $Pb_9(PO_4)_6$ and $Pb_{10}(PO_4)_6X_2$ (X = OH, F, Cl), and independently Engel (1973) precipitated $Pb_{10}(OH)_2(PO_4)_6$, $Pb_{10}O(PO_4)_6$ and $Pb_8M_2(PO_4)_6$ (M = Na, K, Rb, Tl). Brixner, Bierstedt, Jeap & Barkley (1973) reported on the ferroelastic phase transition of monoclinic α-$Pb_3(PO_4)_2$ to hexagonal β-$Pb_3(PO_4)_2$.

In the course of our series of studies on apatite group compounds we obtained single crystals of $Pb_9(PO_4)_6$ and determined its crystal structure.

Powdery lead hydroxyapatite was prepared by a hydrothermal reaction of $Pb(CH_3COO)_2.3H_2O$ and K_2HPO_4 at 473 K for 1 week. This hydroxyapatite was fused at 1363 K and cooled to room temperature, yielding single crystals of a lead phosphate. The crystals are transparent, pale yellow in colour and prismatic in shape with diameters of 0·1–0·2 mm and lengths of 0·2–0·8 mm.

The product was identified to be an apatite from the

0567-7408/80/092128-03$01.00

X-ray powder diffraction pattern. The lattice constants were determined from the 2θ values of 13 reflections with the program *RLC*-3 (Sakurai, 1967). These values, $a = 9{\cdot}826\ (4)$ and $c = 7{\cdot}357\ (3)$ Å, lie between those of $Pb_5OH(PO_4)_3$ ($a = 9{\cdot}877$, $c = 7{\cdot}429$ Å) and $Pb_9(PO_4)_6$ ($a = 9{\cdot}75$, $c = 7{\cdot}20$ Å) listed in the Powder Diffraction File.

Infrared absorption runs of the hydrothermal and the melt products were carried out intensively to establish the existence of OH absorption bands in the range 400 to 4000 cm^{-1}. The stretching band of the hydroxyl group at 3565 cm^{-1} in the former was not observed in the latter, indicating that the hydroxyl groups in the hydrothermal products were lost on heating.

Chemical analysis of the product from the melt was carried out by a gravimetric method. The resulting composition was 76·00 wt% Pb and 23·34 wt% PO_4, corresponding very closely to the chemical formula $Pb_9(PO_4)_6$.

From Weissenberg and precession photographs, the crystal was found to have the Laue symmetry $6/m$ with systematic absences of $00l$ for l odd. The possible space groups are, therefore, restricted to $P6_3/m$ (centrosymmetric) and $P6_3$ (non-centrosymmetric).

Using a spherical crystal of 0·1 mm diameter and Mo $K\alpha$ radiation, we measured the intensities of reflections on an automated four-circle diffractometer (Philips PW 1100/20) in the 2θ–ω scan mode and with a scan speed of 4° min^{-1} in ω. A total of 490 independent reflection data $[|F_o| > 3\sigma(|F_o|)]$ were collected within the range $2\theta \le 80°$. Intensities were corrected for Lorentz and polarization factors. Absorption corrections for a spherical crystal ($\mu = 67{\cdot}8\ mm^{-1}$ for Mo $K\alpha$) were also made.

The refinement was started by assuming the parameters of the Cd atoms in $Cd_5OH(PO_4)_3$ (Hata, Okada, Akao, Aoki & Iwai, 1978) for the Pb atoms. The positions of P and O were determined with the full-matrix least-squares program *LINUS* (Coppens & Hamilton, 1970). Several cycles of calculations converged to give $R = 0{\cdot}043$ and $R_w = 0{\cdot}049$, where R_w is a weighted R in the form $\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2$. For the refinement, anisotropic temperature factors were applied for the Pb and P atoms, and isotropic ones for the O atoms. The weighting scheme employed was $w = 1/(A + B|F_o| + C|F_o|^2 + D|F_o|^3)$. The parameters A, B, C and D were varied so that $w||F_o| - |F_c||^2$ became independent of F_o. The values of A, B, C and D were −8·6212, 6·3114, −0·021548 and 0·00002054 respectively. Preference was given to $P6_3/m$ on the result of the least-squares refinement. The atomic scattering factors for Pb^{2+} and P^{5+} were taken from *International Tables for X-ray Crystallography* (1974) and the scattering factors given by Tokonami (1965) were used for O^{2-}.

Table 1. *Final positional* ($\times 10^4$) *and thermal parameters for* $Pb_9(PO_4)_6$

	x	y	z	B^*_{iso} (Å^2)
Pb(1)	3333	6667	54 (3)	1·38
Pb(2)	2518 (1)	2548 (1)	2500	1·58
P	3951 (7)	196 (7)	2500	1·03
O(1)	3131 (22)	−1638 (23)	2500	1·44
O(2)	5781 (24)	969 (24)	2500	1·63
O(3)	3470 (16)	805 (16)	806 (21)	1·62

* Calculated from the anisotropic thermal parameters according to the expression: $B = 4\,(a^2B_{11} + b^2B_{22} + c^2B_{33} + abB_{12}\cos\gamma)/3$.

The final positional and isotropic thermal parameters are given in Table 1.*

Discussion. The results of the chemical analysis, as mentioned previously, showed a deficiency of Pb from the stoichiometric amount for lead apatite. The multiplicities of the Pb(1) and Pb(2) atoms were varied in the course of refinement, revealing that the deficiency exists only at the Pb(1) site. For the Pb-deficient structure, the chemical formula $Pb_{10-x}O_{1-x}(PO_4)_6$ was assumed in the least-squares refinement; the value of x converged to 1·0, giving a final R value of 0·043. In the structure of the $Pb_9(PO_4)_6$ crystal, there is neither an O atom nor a hydroxyl group in the Pb(2) column and three Pb(1) atoms statistically occupy the four crystallographically equivalent positions ($\frac{1}{3}$,$\frac{2}{3}$,z) in the unit cell. Selected interatomic distances and bond angles are given in Table 2.

There are two crystallographically independent Pb atoms in the unit cell. The Pb(1) atom [4(f) position] is

Table 2. *Interatomic distances* (Å) *and bond angles* (°)

Symmetry code

(0)	x,y,z	(v)	$x-y, x, -z$
(i)	$-y, x-y, z$	(vi)	$y, y-x+1, -z$
(ii)	$x-y, x, \frac{1}{2}+z$	(vii)	$x, y+1, -z$
(iii)	$x, y, \frac{1}{2}-z$	(viii)	$1-x, 1-y, -z$
(iv)	$y-x+1, 1-x, z$		

PO_4 tetrahedra

P—O(1)^0	1·56 (2)
P—O(2)^0	1·56 (2)
P—O(3)^{0,iii} (×2)	1·55 (2)
O(1)—O(2)^0	2·58 (2)
O(1)—O(3)^{0,iii} (×2)	2·57 (2)
O(2)—O(3)^{0,iii} (×2)	2·52 (3)
O(3)—O(3)^{iii}	2·48 (2)
O(1)—P—O(2)^0	111·4 (14)
O(1)—P—O(3)^{0,iii} (×2)	111·3 (7)
O(2)—P—O(3)^{0,iii} (×2)	108·1 (7)
O(3)—P—O(3)^{iii}	106·3 (10)

Environment of metalic atoms

Pb(1)—O(1)^{i,iv,vii} (×3)	2·52 (1)
Pb(1)—O(2)^{v,vi,viii} (×3)	2·76 (1)
Pb(1)—O(3)^{v,vi,viii} (×3)	2·94 (2)
Pb(2)—O(1)^{i}	2·73 (3)
Pb(2)—O(2)^{iv}	2·30 (3)
Pb(2)—O(3)^{0,iii} (×2)	2·63 (2)
Pb(2)—O(3)^{ii,v} (×2)	2·57 (1)
Pb(2)—Pb(2)^{i,vi,viii} (×3)	4·303 (2)

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35290 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

surrounded by nine O atoms [three O(1), three O(2) and three O(3)] at a mean distance of 2·741 Å, whereas the Pb(2) atom [6(*h*) position] is surrounded by six O atoms [O(1), O(2) and four O(3)] at a mean distance of 2·570 Å.

The shape of the $\mathrm{PO_4}$ tetrahedron is almost regular. The mean P—O distance of 1·588 Å is rather long compared with those of other apatites, for example 1·527 Å in $\mathrm{Cd_5OH(PO_4)_3}$ (Hata *et al.*, 1978) and 1·540 Å in $\mathrm{Ba_5Cl(PO_4)_3}$ (Hata, Aoki, Marumo & Iwai, 1979). The O(1)—P—O(2) and O(1)—P—O(3) bond angles are larger than the O(2)—P—O(3) and O(3)—P—O(3)$^{\mathrm{iii}}$ angles, as observed in chlorapatites and hydroxyapatites.

The edge length of the triangle formed by Pb(2) is 4·303 Å, whereas those in $\mathrm{Ba_5Cl(PO_4)_3}$ (Hata *et al.*, 1979) and $\mathrm{Sr_5OH(PO_4)_3}$ (Sudarsanan & Young, 1972) are 4·508 and 4·284 Å respectively. The size of the triangle seems normal for an apatite structure, though anions at the (0,0,*z*) sites are completely missing in the present crystal.

We are very grateful to Professor M. Kato of Tokyo Institute of Technology who allowed us to use an automated four-circle diffractometer. Thanks are due to Associate Professor H. Imai of Tokyo Institute of Technology for his valuable suggestions concerning the IR experiment, and Dr T. Hayashi of Tokyo Institute of Technology for his advice during the chemical analysis. Computations were carried out on the M-180 (HITAC) Computer at the Computation Center of Tokyo Institute of Technology.

References

BHATNAGAR, V. M. (1971). *Rev. Roum. Chim.* **116**(10), 1513–1528.

BRIXNER, L. H., BIERSTEDT, P. E., JEAP, W. F. & BARKLEY, J. R. (1973). *Mater. Res. Bull.* **8**, 497–504.

COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* A**26**, 71–83.

ENGEL, G. (1973). *J. Solid State Chem.* **6**, 286–298.

HATA, M., AOKI, H., MARUMO, F. & IWAI, S. (1979). *Acta Cryst.* B**35**, 2382–2384.

HATA, M., OKADA, K., AKAO, M., AOKI, H. & IWAI, S. (1978). *Acta Cryst.* B**34**, 3062–3064.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

SAKURAI, T. (1967). *Universal Program System for Crystallographic Computations.* Crystallographic Society of Japan.

SUDARSANAN, K. & YOUNG, R. A. (1972). *Acta Cryst.* B**28**, 3668–3670.

TOKONAMI, M. (1965). *Acta Cryst.* **19**, 486.

Acta Cryst. (1980). B**36**, 2130–2132

Barium Diiodate

BY VÁCLAV PETŘÍČEK AND KAREL MALÝ

Institute of Physics, Czechoslovak Academy of Sciences, Na Slovance 2, 180 40 *Praha* 8, *Czechoslovakia*

AND BOHUMIL KRATOCHVÍL,* JANA PODLAHOVÁ AND JOSEF LOUB

Department of Inorganic Chemistry, Charles University, Albertov 2030, 128 40 *Praha* 2, *Czechoslovakia*

(*Received* 21 *March* 1980; *accepted* 22 *April* 1980)

Abstract. $\mathrm{Ba(IO_3)_2}$, monoclinic, $C2/c$, a = 13·638 (9), b = 7·979 (2), c = 9·036 (6) Å, β = 133·62 (4)°, V = 711·8 (6) $\mathrm{Å^3}$, Z = 4, D_x = 4·71, D_m = 4·73 Mg $\mathrm{m^{-3}}$ (pycnometrically under xylene at 296 K), μ(Mo $K\alpha$) = 14·5 $\mathrm{mm^{-1}}$. R = 0·055 for 1036 reflections. The structure consists of pyramidal $\mathrm{IO_3^-}$ anions and $\mathrm{Ba^{2+}}$ cations. The environment of each I atom is completed by two O atoms from two other $\mathrm{IO_3^-}$ ions, so the resulting polyhedron can be described as a distorted trigonal bipyramid. $\mathrm{Ba^{2+}}$ cations have ten O neighbours.

Introduction. Single crystals of $\mathrm{Ba(IO_3)_2}$ were prepared by hydrothermal synthesis from an oversaturated aqueous solution of $\mathrm{Ba(IO_3)_2.2H_2O}$ at 473 K. Systematic absences of the reflections *hkl* for $h + k = 2n + 1$ and *h0l* for $l = 2n + 1$ correspond to space group $C2/c$ or Cc. The former was chosen on the basis of the successful refinement of the structure. The cell dimensions were refined from 28 reflections centred on the diffractometer. A crystal 0·07 × 0·08 × 0·5 mm was chosen for intensity measurements on a Hilger & Watts four-circle diffractometer. Mo $K\alpha$ radiation was used. 1036 independent reflections were measured. Only 999 of them were considered as observed with $I \geq$

---

* Author to whom correspondence should be addressed.

0567-7408/80/092130-03$01.00