Iodo-oxyapatite, the first example from a new class of modulated apatites

Peter Alberius Henning,[a]* Sven Lidin[a] and Václav Petříček[b]

[a]*Inorganic Chemistry, Stockholm University, 106 91 Stockholm, Sweden, and [b]Institute of Physics, Academy of Sciences of the Czech Republic, Prague, Czech Republic. E-mail: peter@inorg.su.se*

Abstract

Iodo-oxyapatite [pentadecacalcium iodide oxide nonaphosphate, $Ca_{15}(PO_4)_9IO$] was synthesized by a flux method and the structure was solved from single-crystal X-ray data. The crystal structure was refined in the space group $P6_3/m$ [$a = 9.567$ (1), $c = 20.754$ (2) Å and $Z = 2$] to wR on F of 0.0459. Iodo-oxyapatite has a typical hexagonal apatite structure but the unit cell is tripled along the hexad owing to ordering of the iodide and oxide ions along this direction.

1. Introduction

The iodo-oxyapatite $Ca_{15}(PO_4)_9IO$ (IOAp) is interesting for several reasons. It is the first reported calcium phosphate apatite with a substantial iodine content and is the first modulated apatite with superstructure ordering along **c**. Additionally, it provides information on the arrangement surrounding the O^{2-} position in oxyapatite, $Ca_{10}(PO_4)_6O$ (OAp), which is similar to that of O^{2-} in IOAp because of the large anion–anion distances along the hexad of the two compounds (McConell & Hey, 1969; Trombe & Montel, 1978; Henning *et al.*, 1996).

Iodoapatite, $Ca_5(PO_4)_3I$, has so far eluded synthesis. A plausible explanation for this is the size of the iodide ion. The corresponding cadmium vanadate apatite, $Cd_5(VO_4)_3I_{1-x}$, does form (Wilson *et al.*, 1977), but only with substantial iodide deficiency ($x \simeq 0.3$). From these considerations the idea of using CaI_2 as a flux for the growth of single crystals of new apatitic phases arose. Attempts to grow oxyapatite by this method resulted in iodo-oxyapatite, which may be seen as an intergrowth between the desired oxyapatite and the elusive iodoapatite.

2. Experimental

Calcium oxide, CaO, was mixed with stoichiometric amounts of tricalcium phosphate, $Ca_3(PO_4)_2$, and a large excess of calcium iodide, CaI_2. The syntheses were performed in platinum crucibles sealed in evacuated quartz tubes at 1123 K for 48 h. Excess CaI_2 was removed by dissolving it in water. The monophasic residue consisted of hexagonal needles of the title compound.

A Jeol 3010 electron microscope was used for the electron-diffraction experiments. The maximum accelerating voltage was 300 kV and the microscope was equipped with a double-tilt holder that could be tilted by $\pm 20°$.

The single-crystal X-ray diffraction experiment was performed on a Stoe image plate diffraction system (IPDS; Stoe, 1987) equipped with a Siemens rotating anode. Details are given in Table 1. *JANA*98 was used for the refinement (Petrícek, 1994).

3. Refinement from single-crystal diffraction data

The refinement was conducted in three distinct steps:

(i) The average structure was refined from the basic reflections.

(ii) A modulated structure was refined from the whole data set.

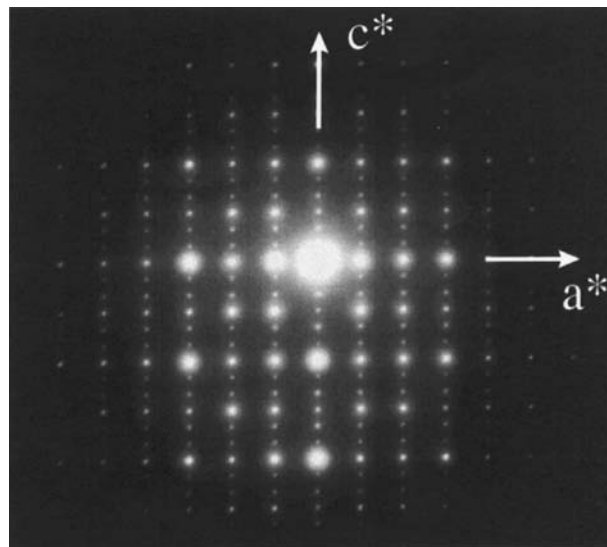(iii) Finally, the modulated structure was transformed to a supercell and refined.

Fig. 1. A selected-area electron-diffraction pattern of IOAp along [010]. Note the intensities of satellites surrounding $l_{subcell} = 2n$ and $l_{subcell} = 2n + 1$ (acceleration voltage 300 kV).

Table 1. *Experimental details*

Crystal data

Chemical formula	$Ca_{15}(PO_4)_9IO$
Chemical formula weight	1598.8
Cell setting	Hexagonal
Space group	$P6_3/m$
a (Å)	9.567 (1)
c (Å)	20.754 (2)
V (Å^3)	1645.07
Z	2
D_x (Mg m^{-3})	3.227
Radiation type	Mo $K\alpha$
Wavelength (Å)	0.7107
No. of reflections for cell parameters	5000
θ range (°)	1.96–23.9
μ (mm^{-1})	3.887
Temperature (K)	293
Crystal form	Hexagonal rod
Crystal size (mm)	$0.18 \times 0.025 \times 0.025$
Crystal colour	Colourless

Data collection

Diffractometer	Stoe IPDS
Data collection method	φ rotation scans
Absorption correction	Numerical from crystal shape (*X-red*; Stoe, 1996)
T_{min}	0.8591
T_{max}	0.9169
No. of measured reflections	878
No. of independent reflections	878
No. of observed reflections	419
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.0836
θ_{max} (°)	23.9
Range of h, k, l	$-8 \rightarrow h \rightarrow 0$
	$0 \rightarrow k \rightarrow 10$
	$0 \rightarrow l \rightarrow 23$
Intensity decay (%)	0

Refinement

Refinement on	F
R	0.0452
wR	0.0459
S	1.29
No. of reflections used in refinement	878
No. of parameters used	72
Weighting scheme	$w = 1/[\sigma^2(F) + 0.0004F^2]$
$(\Delta/\sigma)_{max}$	0.0001
$\Delta\rho_{max}$ (e Å^{-3})	2.50
$\Delta\rho_{min}$ (e Å^{-3})	−2.48
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C)

The IOAp structure was first refined as an average apatite structure using only the subcell reflections and the atomic parameters of bromoapatite, BrAp, (Elliott *et al.*, 1981) as the starting parameters.

In the next step a modulated structure was refined using the whole data set. The superstructure satellites were found in planes perpendicular to $\mathbf{c}^*$ at (h k l/3). The modulation vector $\mathbf{q}$ was set to $2/3\mathbf{c}^*$ in the four-dimensional space group $P6_3/m$ (00γ). The $\mathbf{q}$ vector was set to $2/3\mathbf{c}^*$ since the satellites were stronger close to the

weak *hkl l* = odd planes instead of close to the *hkl l* = $2n$ planes (Fig. 1). Of the 419 unique significant $[I > 2\sigma(I)]$ reflections, 186 were satellites of the first order.

The modulation was first treated as noncommensurate neglecting satellites of higher order, but with limited success.

Next, an attempt was made to refine the structure as being commensurately modulated including higher-order satellites coherently overlapping main reflections as well as superstructure satellites. In the following discussion parameters in the subcell setting are denoted by the subscript 0 (*e.g.* z_0 corresponds to the z coordinate in the subcell). The I atoms were occupationally as well as positionally modulated, the rest of the atoms were positionally modulated only. In a first attempt only one I-atom position was introduced (at $z_0 = 0$) under the assumption that the apatite was pure IAp with ordered vacancies along the c axis giving the superstructure. This description did not fit the electron density along the c axis and a second I-atom position was introduced at $z_0 = 1/4$. The site-occupancy factors were refined for the two I atoms to a total occupancy well below 1. The occupancy factors and the position of the second I atom led to the conclusion that this atom was actually an oxygen. The new refinement of the occupancy factors for the modulated I and O atoms on the c axis led to an occupancy factor of approximately 1/3 for each of the two atoms and the sum of the negative charges was 1 per formula unit, as expected. The refinement of the IOAp structure in the commensurate setting was carried out using 65 parameters to wR(obs) = 0.0385. The largest root-mean-square deviations of the electron density in the final difference Fourier map were 2.68 and −3.10 e Å^{-3}, mainly because of difficulties in modelling the anions along the hexad. The modulated approach is successful and gives a good picture of the effect of the modulation upon the apatite structure and how the amplitude of the positional modulation decreases with increasing distance from the c axis. However, the interpretation of the behaviour of the anions within the iodine–oxygen column is not straightforward and hence a transformation of the parameters to a conventional supercell setting was performed.

The superstructure was refined with a cell tripled along the c axis in the space group $P6_3/m$ [$a = 9.567$ (1), $c = 20.754$ (2) Å and $Z = 2$]. The coordinates are from this point related to the supercell ($c_{supercell} = 3 \times c_{subcell}$). In the supercell setting the crystal structure was first refined with the I atom at $z = 0$ and the O atom at $z = 1/4$. After evaluation of a difference Fourier synthesis ($F_{obs} - F_{calc}$) it was concluded that there is a disorder within the iodine–oxygen columns. There are six halogenide and O-atom sites each per unit cell and in perfect IOAp only one-third of them should be occupied (Fig. 2a). However, owing to disorder in the stacking sequence of the anions within the column along the hexagonal axis (Figs. 2b,c), the anions are split over two positions each.

Table 2. *Site-occupancy factors, fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$)*

$$U_{\mathrm{eq}} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	Occupancy	x	y	z	U_{eq}
O(11)	1	0.473 (1)	0.590 (1)	1/4	0.028 (3)
O(12)	1	0.4599 (9)	0.5848 (8)	0.5930 (5)	0.028 (3)
O(21)	1	0.481 (1)	0.328 (1)	1/4	0.010 (2)
O(22)	1	0.4886 (8)	0.3353 (8)	0.5830 (4)	0.010 (2)
O(31)	1	0.268 (1)	0.360 (1)	0.1901 (5)	0.034 (2)
O(32)	1	0.2831 (9)	0.375 (1)	0.5186 (4)	0.034 (2)
O(33)	1	0.245 (1)	0.318 (1)	0.8634 (5)	0.034 (2)
P(11)	1	0.3731 (5)	0.4048 (5)	1/4	0.0063 (7)
P(12)	1	0.3690 (3)	0.3999 (3)	0.5826 (2)	0.0063 (7)
Ca(11)	1	1/3	2/3	0.1665 (2)	0.0103 (5)
Ca(12)	1	1/3	2/3	0.5008 (3)	0.0103 (5)
Ca(13)	1	1/3	2/3	0.8297 (2)	0.0103 (5)
Ca(21)	1	0.2435 (5)	0.0041 (4)	1/4	0.028 (2)
Ca(22)	1	0.2765 (3)	0.0144 (3)	0.5859 (1)	0.018 (1)
I(11)	0.7 (1)	0	0	0	0.0211 (9)
I(12)	0.174 (3)	0	0	0.1716 (6)	0.0211 (9)
O(41)	0.35 (2)	0	0	0.237 (3)	0.0211 (9)
O(42)	0.14 (2)	0	0	0.384 (6)	0.0211 (9)

The sum of the occupancy factors multiplied by the negative charge of the I and O atoms was held constant at 6 per unit cell during the refinement, but no other restrictions were placed on the occupancy factors for the I and O atoms. Nevertheless, the occupancy factor for I(1) at $z = 0$ is the same as for the O(41) split position around $z = 1/4$.

During the refinement the displacement factors were restricted to be equal for atoms originating from the same site in the average cell, except for Ca(21) and Ca(22). Finally, anisotropic refinement was carried out; R/wR decreased from 0.085/0.089 to 0.045/0.046. The atoms showed only small deviations from spherical displacement with the exception of atoms lying on the c axis. The atom-site parameters are summarized in Table 2†.

4. Structural description

The iodo-oxyapatite structure is very closely related to the hydroxyapatite [$Ca_5(PO_4)_3O$, OHAp] structure (Kay *et al.*, 1964) (Fig. 3). The phosphate tetrahedra and Ca(1) are at almost the same positions as in OHAp, the P—O distances vary between 1.52 (1) and 1.55 (1) Å and the 6 + 3 coordinated calcium Ca(1)—O distances vary between 2.44 (1) and 2.72 (1) Å. The differences between IOAp and OHAp become larger the closer to the c axis the atoms are. The second Ca position in apatite, Ca(2), is split into Ca(21) and Ca(22) in the supercell. The Ca(21) triangle with O(41) at its centre behaves like Ca(2) in OHAp with a Ca—Ca distance of 4.001 (7) Å and the empty Ca(22) triangle expands like Ca(2) in bromoapatite or chloroapatite (Elliott *et al.*, 1981; Mackie *et al.*, 1972) with the O-atom site empty and a Ca—Ca distance of 4.400 (5) Å (Fig. 4). The anions on the c axis are distributed approximately 5 Å apart with I$^-$ at $z = 0$ and O^{2-} at $z = 0.23$. For a structure free from stacking faults this means that there are no short contacts along the c axis. The coordination and
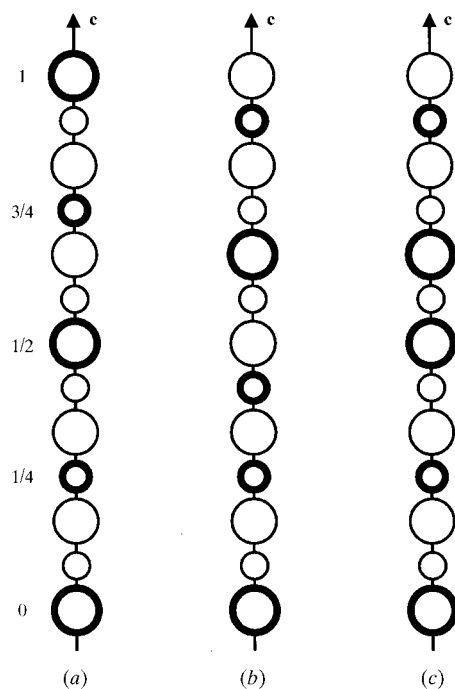

Fig. 2. The packing of anions along the c axis. Large circles represent I-atom positions, small circles represent O-atom positions and bold circles represent occupied sites. (*a*) Ideally ordered iodo-oxyapatite; (*b*) a plausible stacking fault where two O atoms are packed one after the other; (*c*) a stacking fault where two I atoms are stacked one after the other.

† Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS0009). Services for accessing these data are described at the back of the journal.

position of I is the same as for Br in bromoapatite (Elliott *et al.*, 1981).

The disorder in the stacking sequence of anions along the *c* axis may be explained by the relatively large anion–anion distance (5 Å) in ideal IOAp. One plausible mechanism is that, for example, two O atoms are introduced one after the other (on O-atom sites lying 3 Å apart), the overall charge neutrality being restored by a vacancy higher up the column. The large displacement parameters U^{33} ($U^3/U^1 \simeq 17$) on I(11), I(12), O(41) and O(42) may be explained by the same mechanism used for explaining the large U^{33} value for Cl and F in (F,Cl)Ap (Mackie & Young, 1974). The stacking faults mentioned above give short O⋯O or I⋯I distances, pushing them apart. This is seen as large U^{33}

Fig. 3. A view of OHAp projected along [001]. Phosphate tetrahedra are represented as shaded triangles, large circles are Ca^{2+} ions and small circles are OH^- ions.

Ca(21), $z = 1/4$

O^{2-}, $z = 0.23$
vacancy, $z = 0.58$

Ca(22), $z = 0.59$

Fig. 4. An *ORTEP*II (Johnson, 1976) plot of Ca(2) in iodo-oxyapatite. Atoms are represented as 50% probability displacement ellipsoids.

displacement factors. The occupancy factors of I(12) and O(42) give an indication of how frequently the stacking faults occur. The relatively large anharmonicity on Ca(21) (Fig. 4) is a result of the partial occupancy of O(41). This is really a split position, the Ca triangle contracting when O(41) is present and expanding when this atom is absent.

5. Concluding remarks

The structure of iodo-oxyapatite is closely related to that of oxyapatite since both structures contain Ca(2) triangles filled with O^{2-} ions in parallel with empty Ca(2) triangles. The IOAp structure validates the assumption made about the behaviour of Ca around the vacancy in OAp (Henning *et al.*, 1996; Alberius Henning *et al.*, 1999). In OAp the Ca—Ca distance around the vacancy is 4.34 Å, which is close to the Ca—Ca distance of 4.400 (4) Å in IOAp. On the other hand, the Ca—Ca distance around the O^{2-} ion [4.001 (7) Å] is a bit shorter than the Ca—Ca distance around OH^- in OHAp (4.08 Å), which is in accordance with the higher absolute charge of the O^{2-} ion, which attracts the Ca^{2+} ion more than OH^- does. The O^{2-} ion is located 0.35 Å away from the centre of the Ca triangle, like the OH^- ion in OHAp, and not in the centre as was suggested in the OAp model.

Iodo-oxyapatite is the first example from a new class of modulated apatites where the modulation results from the stacking of anions of different charge along the hexagonal channel. No report of an apatite modulated along **c** giving an ordered superstructure is found in the literature. However, some cadmium apatites have been reported previously with anion vacancies along the hexagonal channel (Wilson *et al.*, 1977) and an electron-diffraction study of these materials showed additional order along **c** as diffuse scattering (this will be the subject of another paper). This modulation is due to ordered vacancies.

We are expecting a rich flora of apatites modulated as a result of ordering of mono- and divalent anions or mono- and trivalent anions along the hexagonal channel.

References

Alberius Henning, P., Landa-Cánovas, A. R., Larsson, A.-K. & Lidin, S. (1999). *Acta Cryst.* B**55**, 170–176.

Elliott, J. C., Dykes, E. & Mackie, P. E. (1981). *Acta Cryst.* B**37**, 435–438.

Henning, P., Landa-Cánovas, A. R., Larsson, A.-K. & Lidin, S. (1996). *Proceedings of EUREM-11*, Dublin, Ireland, Vol. 3, 91–92.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kay, M. I., Young, R. A. & Posner, A. S. (1964). *Nature*, **204**, 1050–1062.
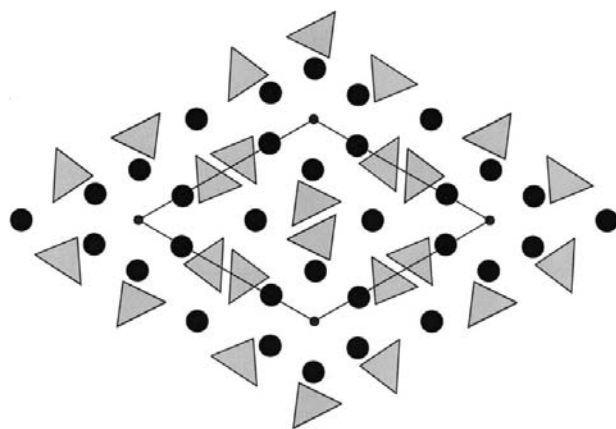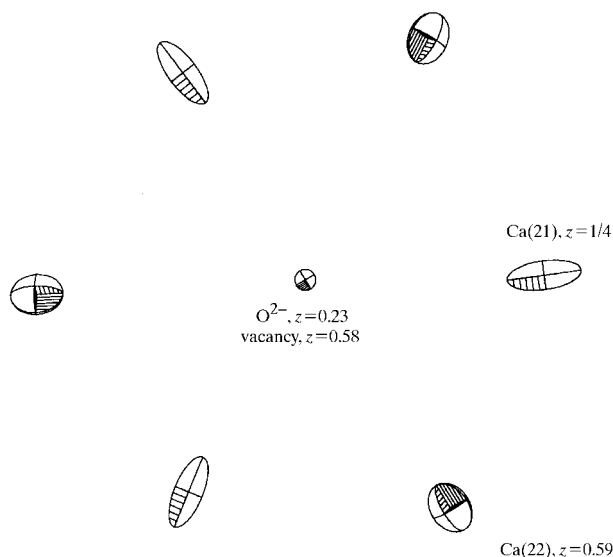
McConell, D. & Hey, M. H. (1969). *Mineral. Mag.* **37**, 301–303.

Mackie, P. E., Elliott, J. C. & Young, R. A. (1972). *Acta Cryst.* **B28**, 1840–1848.

Mackie, P. E. & Young, R. A. (1974). *J. Solid State Chem.* **11**, 319–329.

Petrícek, V. (1994). *JANA. Crystallographic Computing System.* Institute of Physics, Academy of Sciences of the Czech Republic, Prague, Czech Republic.

Stoe (1987). *IPDS Software Manual.* Version 2.87. Stoe, Darmstadt, Germany.

Stoe (1996). *X-red. Data Reduction Program for Stadi-4 and IPDS.* Stoe, Darmstadt, Germany.

Trombe, J. C. & Montel, G. J. (1978). *J. Inorg. Nucl. Chem.* **40**, 15–21.

Wilson, A. J. C., Sudarsanan, K. & Young, R. A. (1977). *Acta Cryst.* **B33**, 3142–3154.