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Lead bismuth calcium sodium phosphate: $Pb_{4.6}Bi_{0.4}Ca_{2.6}Na_{2.4}(PO_4)_6$

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The title compound, lead bismuth calcium sodium phosphate, $Pb_{4.6}Bi_{0.4}Ca_{2.6}Na_{2.4}(PO_4)_6$ crystallizes in the apatite structure type, with vacancies in sites $2a$ or $2b$ that are normally occupied by anions. The fact that the Bi and Pb ions are mainly localized in the $6h$ sites confirms the electron lone-pair influence on the apatite structure.

Comment

Because of their biological occurrences and their chemical properties, apatite-type compounds have been widely investigated. The general formula of these compounds is $M_{10}(YO_4)_6X_2$ (M is an alkaline earth metal, lead or a rare earth metal *etc.*, Y = P, As, Si, Ge, S, V or Mn, and X = OH, a halogen, 0.5O, 0.5S or $0.5CO_3$). Many studies have reported the syntheses, structures, thermal stabilities, and IR and Raman spectroscopy of these compounds (El Feki *et al.*, 2000). Apatite crystallizes in the hexagonal system (space group $P6_3/m$), with cations occupying the $4f$ and $6h$ sites in the crystal lattice. Lead apatites, with the general formula $Pb_8M_2(PO_4)_6$, have been prepared, M being a monovalent ion, usually Na, K or Rb (Mayer *et al.*, 1981). Apatites with mixed anions, such as $Pb_{10}(PO_4)_4(SiO_4)_2$, which exhibit anionic lacunae, have also been investigated (Merker & Wondratschek, 1960). Moreover, chemical and physical studies have been performed on lacunary lead apatite with calcium partially substituted for lead, $Pb_6Ca_2Na_2(PO_4)_6$, which has vacancies in the Y-anion sites (Naddari *et al.*, 2002).

We present here a structural determination of a lacunary lead apatite with calcium and bismuth partially substituted for lead, *viz*. $Pb_{4.6}Bi_{0.4}Ca_{2.6}Na_{2.4}(PO_4)_6$ (Fig. 1). This formula diverges from that expected and reveals that, during the heating process, a loss of PbO and Bi_2O_3 occurs. The title compound is isostructural with $Pb_6Ca_2Na_2(PO_4)_6$ (Naddari *et al.*, 2003), the best refinement giving the formula $[Pb_{0.12}Ca_{2.59}Na_{1.29}]^{4f}[Pb_{4.49}Bi_{0.40}Na_{1.09}]^{6h}(PO_4)_6$. The Bi/Pb allotment is arbitrary because, as a result of the quality of the data, X-ray analysis cannot allow us discriminate between Bi and Pb atoms; there is a difference of only one electron between them. However, constraint of the electroneutrality helps to obtain the Bi^{3+}-ion quantity. Effectively, when M^{3+} ions are substituted for M^{2+} ions, a charge compensation mechanism occurs and two processes may be invoked, *viz*.

$$3M^{2+} \rightarrow 2M^{3+} + 1 \text{ vacancy}$$

or

$$2M^{2+} \rightarrow 1M^{3+} + 1M^{+}.$$

The first mechanism is unrealistic, because Na atoms were introduced in the synthesis since we assumed that the second mechanism would occur. Moreover, the formula given by the structure solution confirms this assumption. The $4f$ site is preferentially occupied by Na or Ca atoms. Nevertheless, a small amount of a heavy atom is found in this site, although the corresponding z coordinate is found at $z = \frac{1}{4}$. For structures with lead in this site [*e.g.* $Pb_8M_2(PO_4)_6$], the z coordinate is moved to 0.29, which behaviour has been attributed to lone-pair interactions. We may thus assume that, if there is a Pb atom in this site, it is so diluted that interactions are unobservable. The $6h$ site is filled by Pb, Bi and Na atoms. Although the amount of sodium in this site (18%) appears important, the Na-atom distribution in the $6h$ and $4f$ sites (45.8 and 54.2%, respectively) does not match the statistical distribution (60 and 40%, respectively), thus revealing that sodium prefers the $4f$ site. Previous studies explained that lone-pair interactions stabilize the triangular shape of atoms with an electron lone pair. Thus, in the title compound, triangles of Pb_3^{2+} to Bi_3^{3+}, with substitutions in between, are expected. Sodium, which has the lowest electric charge, can form triangles of lower repulsive energy than can calcium, which may explain why calcium is not observed in the $6h$ site. Assuming such a triangular arrangement, we propose a supercell made of 15

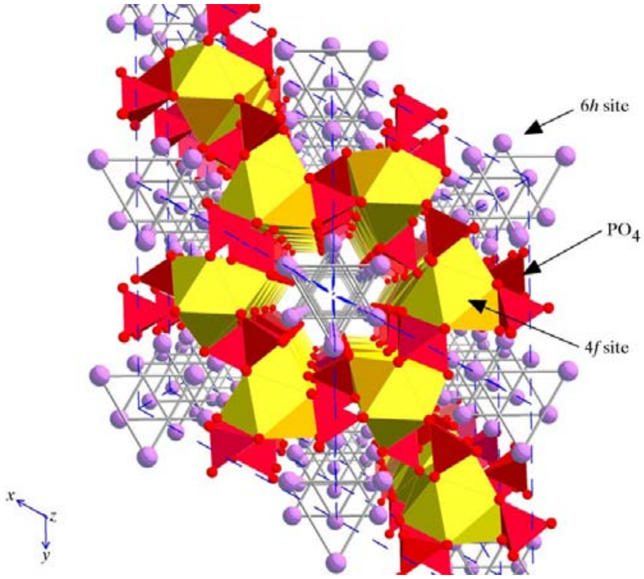

Figure 1
A view of the structure of the title compound.

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cells stacked in the [001] direction, which allows a composition of 50 Pb/Bi triangles and 11 Na triangles. The PO_4^{3-} tetrahedra, which occupy 6*h* positions similar to those occupied by the *M*(6*h*) cations, form an expanded triangular configuration. Adjacent *M*(4*f*) and *M*(6*h*) polyhedra are linked *via* phosphate O atoms. Comparison of the PO_4^{3-} tetrahedra in our compound and in $Pb_8Na_2(PO_4)_6$ (Ternane *et al.*, 2000) shows a slight shortening of the average P—O distance [1.533 (14) and 1.545 (8) Å, respectively]. The P—O2 distance appears to be the shortest P—O bond, and this situation can be attributed to the fact that atom O2 is mainly connected to two *M*(4*f*) sites, which contain the M^+ cation, while atoms O1 and O3 principally interact with the *M*(6*h*) sites, which are preferentially occupied by M^{3+} and M^{2+} cations. As expected, the average O—P—O angle is 109.41°, but the standard error (3.0°) confirms that distortion of the tetrahedron occurs. Angles that include the O2—P bond are greater than the other O—P—O angles [112.64 (14) and 106.0 (3)°, respectively; Table 1], thus confirming the P—O2 axial deformation and the influence of substitution in the cationic sites on the PO_4 distortion.

Table 1
Selected geometric parameters (Å, °).

$Pb1—O2^{i}$	2.418 (3)	$Pb2—O3^{iv}$	2.548 (3)
Pb1—O1	2.526 (3)	$Pb2—O2^{v}$	2.948 (4)
$Pb1—O3^{ii}$	2.824 (4)	P—O2	1.515 (4)
Pb2—O1	2.310 (4)	P—O3	1.534 (3)
$Pb2—O3^{iii}$	2.466 (3)	P—O1	1.551 (4)
O2—P—O3	112.64 (14)	O2—P—O1	111.0 (2)
$O3^{vi}—P—O3$	106.0 (3)	O3—P—O1	107.11 (17)

Symmetry codes: (i) $1+y, 1-x+y, -z$; (ii) $1-y, x-y, \frac{1}{2}-z$; (iii) $1-x, -y, 1-z$; (iv) $1-y, x-y, z$; (v) $1-x+y, -x, z$; (vi) $x, y, \frac{1}{2}-z$.

Experimental

Crystals of the title compound were obtained from a mixture of Na_2CO_3, $(BiO)_2CO_3$, PbO and $(NH_4)_2HPO_4$, with stoichiometry according to the formula $Pb_4BiCa_2Na_3(PO_4)_6$. A series of stages of heating followed by grinding were performed until a pure apatite was obtained. Between each stage, the temperature was increased by 50 K, up to a maximum of 1373 K. Crystals were obtained after heating for 1 h at 1373 K and slow cooling at 20 K h^{-1} to 1173 K. IR spectroscopic analysis did not reveal any carbonate absorption in the compound.

Crystal data

$Pb_{4.6}Bi_{0.4}Ca_{2.6}Na_{2.4}(PO_4)_6$
$M_r = 1768.64$
Hexagonal, $P6_3/m$
$a = 9.5953$ (6) Å
$c = 7.0418$ (4) Å
$V = 561.48$ (6) Å^3
$Z = 1$
$D_x = 5.231$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 152 reflections
$\theta = 5.0$–$48.0°$
$\mu = 38.79$ mm^{-1}
$T = 293$ (2) K
Hexagonal needle, colourless
0.20 × 0.04 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: Gaussian (Coppens *et al.*, 1965)
$T_{min} = 0.066$, $T_{max} = 0.372$
17 792 measured reflections
1863 independent reflections
1199 reflections with $I > 2\sigma(I)$
$R_{int} = 0.090$
$\theta_{max} = 48.0°$
$h = -16 \rightarrow 20$
$k = -20 \rightarrow 19$
$l = -14 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.075$
$S = 1.04$
1863 reflections
44 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0119P)^2 + 3.2549P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.030$
$\Delta\rho_{max} = 3.05$ e Å^{-3}
$\Delta\rho_{min} = -2.45$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0019 (4)

The main difficulty arises from the occupation of both 4*f* and 6*h* cationic sites by Pb, Bi, Ca or Na atoms. Nevertheless, Fourier summation revealed that the electron density was much more intense in the 6*h* site than in the 4*f* site, thus inferring that the 6*h* site is preferentially occupied by heavy atoms and the 4*f* site is occupied by light atoms. In order to obtain the distribution of the various atoms in each site, constraints on occupancy (assuming full occupation) and electroneutrality were applied. Any attempt to remove the constraints caused the refinement to diverge, which behaviour can be attributed to the number of different kinds of atom in one site. Because of the very large absorption coefficient, weak reflections were poorly measured, thus producing a large residual near the heavy atoms (Pb or Bi) in the 6*h* site.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DIRAX*/*LSQ* (Duisenberg, 1992); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *CrystalMaker* (CrystalMaker Software, 1999); software used to prepare material for publication: *PLATON* (Spek, 2003).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1662). Services for accessing these data are described at the back of the journal.

References

Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* **18**, 1035–1038.
CrystalMaker Software (1999). *CrystalMaker.* Version 4.4. CrystalMaker Software, Bicester, England.
Duisenberg, A. J. M. (1992). *J. Appl. Cryst.* **25**, 92–96.
Duisenberg, A. J. M., Kroon-Batenburg, L. M. J. & Schreurs, A. M. M. (2003). *J. Appl. Cryst.* **36**, 220–229.
El Feki, H., Naddari, T., Savariault, J. M. & Ben Salah, A. (2000). *J. Solid State Sci.* **2**, 725–733.
Mayer, I., Cohen, S. & Matalon, J. R. (1981). *J. Solid State Chem.* **36**, 271–274.
Merker, L. & Wondratschek, H. Z. (1960). *Kristallografiya*, **113**, 475.
Naddari, T., El Feki, H., Savariault, J. M., Salles, P. & Ben Salah, A. (2003). *J. Solid State Ionics*, **158**, 157–166.
Naddari, T., Hamdi, B., El Feki, H., Savariault, J. M. & Ben Salah, A. (2002). *Mater. Res. Bull.* **38**, 221–230.
Nonius (1998). *COLLECT.* Nonius BV, Delft, The Netherlands.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Ternane, R., Ferid, M., Kbir-Ariguib, N. & Trabelsi-Ayedi, M. (2000). *J. Alloys Compd*, **308**, 83–92.