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Rietveld refinement of Ba₅(AsO₄)₃Cl from high-resolution synchrotron data

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 Key indicators: powder synchrotron study; $T = 298$ K; mean $\sigma(\text{As}-\text{O}) = 0.040$ Å; R factor = 0.059; wR factor = 0.082; data-to-parameter ratio = 22.1.

The apatite-type compound Ba₅(AsO₄)₃Cl, pentabarium tris[arsenate(V)] chloride, has been synthesized by ion exchange at high temperature from a synthetic sample of mimetite (Pb₅(AsO₄)₃Cl) with BaCO₃ as a by-product. The results of the Rietveld refinement, based on high resolution synchrotron X-ray powder diffraction data, show that the title compound crystallizes in the same structure as other halogenoapatites with general formula A₅(YO₄)₃X (A = divalent cation, Y = pentavalent cation, X = Cl, Br) in space group *P6₃/m*. The structure consists of isolated tetrahedral AsO₄³⁻ anions (*m* symmetry), separated by two crystallographically independent Ba²⁺ cations that are located on mirror planes and threefold rotation axes, respectively. The Cl⁻ anions are at the *2b* sites ($\bar{3}$ symmetry) and are located in the channels of the structure.

Related literature

For crystal chemistry of apatites, see: Mercier *et al.* (2005); White & ZhiLi (2003); Wu *et al.* (2003). For powder diffraction data on Ba-containing As-apatites, see: Kreidler & Hummel (1970); Dunn & Rouse (1978). Atomic coordinates as starting parameters for the Rietveld (Rietveld, 1969) refinement of the present phases were taken from Chengjun *et al.* (2005); Dai *et al.* (1991); de Villiers *et al.* (1971). For related Ba–Cl-apatites, see: Đorđević *et al.* (2008); Hata *et al.* (1979); Reinen *et al.* (1986); Roh & Hong (2005); Schiff-Francois *et al.* (1979). For synthetic work, see: Baker (1966); Essington (1988); Harrison *et al.* (2002).

Experimental

Crystal data

 As₃Ba₅ClO₁₂
 $M_r = 1138.85$
 Hexagonal, *P6₃/m*
 $a = 10.5570$ (1) Å
 $c = 7.73912$ (8) Å
 $V = 746.98$ (1) Å³
 $Z = 2$
 Synchrotron radiation

 $\lambda = 0.998043$ Å
 $\mu = 56.07$ (1) mm⁻¹
 $T = 298$ K
 Specimen shape: cylinder
 $40 \times 0.7 \times 0.7$ mm
 Specimen prepared at 100 kPa
 Specimen prepared at 1258 K
 Particle morphology: powder, white

Data collection

 In-house design diffractometer
 Specimen mounting: capillary
 Specimen mounted in transmission mode

 Scan method: step
 Absorption correction: none
 $2\theta_{\min} = 2$, $2\theta_{\max} = 70^\circ$
 Increment in $2\theta = 0.01^\circ$

Refinement

 $R_p = 0.059$
 $R_{wp} = 0.082$
 $R_{exp} = 0.067$
 $R_B = 0.090$
 $S = 1.23$
 Excluded region(s): 2-6 degrees 2θ .

 Profile function: Fundamental
 Parameters
 464 Bragg reflections
 21 parameters
 Preferred orientation correction: none

Table 1

Selected geometric parameters (Å, °).

Ba1–O1	2.67 (5)	Ba2–O1 ^v	3.14 (4)
Ba1–O2 ⁱ	2.81 (4)	Ba2–Cl1 ^{iv}	3.281 (5)
Ba1–O3 ⁱ	3.12 (3)	As1–O3	1.64 (2)
Ba2–O2 ⁱⁱ	2.59 (4)	As1–O1	1.70 (8)
Ba2–O3 ⁱⁱⁱ	2.62 (4)	As1–O2	1.70 (4)
Ba2–O3 ^{iv}	3.05 (4)		
O3–As1–O3 ^{vi}	118 (2)	O3–As1–O2	108 (2)
O3–As1–O1	108 (1)	O1–As1–O2	106 (2)

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

Data collection: local software; cell refinement: *CELREF* (Laugier & Bochu, 2003); data reduction: local software; method used to solve structure: coordinates taken from a related compound; program(s) used to refine structure: *TOPAS* (Coelho, 2000); molecular graphics: *Balls and Sticks* (Kang & Ozawa, 2003); software used to prepare material for publication: *publCIF* (Westrip, 2008).

AMTB acknowledges the use of the EPSRC's Chemical Database Service at Daresbury (Fletcher *et al.*, 1996). AMTB also acknowledges the referees and Co-editor whose suggestions and comments helped to improve this paper.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2188).

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supplementary materials

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Rietveld refinement of Ba₅(AsO₄)₃Cl from high-resolution synchrotron data

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Comment

Apatites are minerals and synthetic compounds with general formula $A_5(YO_4)_3X$, containing tetrahedrally coordinated YO_4^{3-} anions (Y = pentavalent cation) and a monovalent anion X such as F^- , Cl^- or OH^- . The divalent cations frequently belong to the alkaline earth group, but other cations like Pb^{2+} are also known. For a review of the structures and crystal-chemistry of these materials, see Mercier *et al.* (2005) and White & Dong (2003). Apatites containing arsenic (As-apatites) are of interest as hosts for storage of arsenic removed from contaminated water (Harrison *et al.*, 2002). Powder diffraction data for the Ba containing As-apatites Ba₅(AsO₄)₃Cl (Kreidler & Hummel, 1970) and for (Ba_{2.25}Ca_{1.65}Pb_{1.16}Fe_{0.06}Mg_{0.06})[(AsO₄)_{2.56}(PO₄)_{0.3}]Cl_{1.09} (mineral name morelandite; Dunn & Rouse, 1978) were indexed in space group $P6_3/m$. Related crystal structures have also been reported for Ba₅(AsO₄)₂SO₄S (Schiff-Francois *et al.*, 1979) and (Sr_{1.66}Ba_{0.34})(Ba_{2.61}Sr_{0.39})(AsO₄)₃Cl (Dordevic *et al.*, 2008). The crystal structure of Ba₅(AsO₄)₃Cl in space group $P6_3/m$ is reported in the present communication.

Table 1 shows refined interatomic distances and angles for the Ba₅(AsO₄)₃Cl structure. The averaged Ba1—O and Ba2—O distances of respectively 2.87 Å and 2.84 Å are similar to those in other Ba and Cl containing apatites. In comparison, the average Ba1—O and Ba2—O distances are 2.84 Å and 2.78 Å for Ba₅(VO₄)₃Cl (Roh & Hong, 2005), 2.83 Å and 2.79 Å for Ba₅(PO₄)₃Cl (Hata *et al.*, 1979) and 2.83 Å and 2.76 Å for Ba₅(MnO₄)₃Cl (Reinen *et al.*, 1986). The As—O distances are characteristic for tetrahedral AsO₄ units. The O—As—O angles deviate significantly from the ideal tetrahedral angle of 109.5°, indicating a strong distortion.

The refined lattice parameters for Ba₅(AsO₄)₃Cl are similar to the previously published parameters of $a = 10.54$ Å, $c = 7.73$ Å given by Kreidler & Hummel (1970). A study of 108 existing and predicted apatites with different compositions made use of elemental radii to calculate their lattice parameters (Wu *et al.*, 2003). Only 52 of these compositions had known lattice parameters. The predicted lattice parameters for Ba₅(AsO₄)₃Cl were $a = 10.3979$ Å, $c = 7.6105$ Å. These predicted parameters are respectively 1.51% and 1.66% smaller than the measured lattice parameters, and only 2 of the 52 apatite compositions had bigger differences between observed and calculated lattice parameters.

Fig. 1 shows the Rietveld difference plot for the present refinement. The crystal structure of Ba₅(AsO₄)₃Cl, showing the isolated tetrahedral AsO₄³⁻ anions separated by Ba²⁺ cations and Cl⁻ anions, is displayed in Fig. 2.

Experimental

This work was part of an attempt to synthesize analogues of Pb₅(AsO₄)₃Cl (mimetite) with Pb²⁺ substituted by alkaline earth cations. All starting materials were well crystallized solids. Pb₅(AsO₄)₃Cl was precipitated by titration of 0.1M Na₂HAsO₄ into a well stirred, saturated PbCl₂ solution at room temperature (procedure modified from methods of Baker (1966) and

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Essington (1988)). The molar ratio of Pb:As was slightly greater than 5:3, allowing for excess PbCl₂ during the precipitation. A very fine-grained pure solid formed immediately, which was then separated, washed, and dried. Typically, five de-ionized water washes were needed to reduce the conductivity of the wash water to < 50 μS·cm⁻¹. Ba₅(AsO₄)₃Cl was successfully synthesized by ion exchange of Pb₅(AsO₄)₃Cl with molten BaCl₂ at 1258 K (modified from the method given by Kreidler & Hummel (1970)). Two fusions were required to completely eliminate formation of Pb containing solid solutions and to yield the Pb free title compound. Excess metal in the form of BaCl₂ was removed from the solids by repeated washing with de-ionized water followed by centrifugation and filtration to separate the solid from the solution.

Refinement

The powdered sample was loaded into a 0.7 mm diameter borosilicate capillary, prior to high-resolution synchrotron X-ray powder diffraction data collection using station 9.1 of the Daresbury Synchrotron Radiation Source. The beam on the sample was 13 mm wide and 1.2 mm high. 9 powder datasets were collected, all were with a step with of 0.01°/2θ and a counting time of 2 s per point. Three of these datasets were collected between 5–70°/2θ, two between 30–70°/2θ, two between 40–70°/2θ, one between 31.73–70°/2θ and one between 2–13.2°/2θ. All of these data were summed and normalized to account for decay of the synchrotron beam with time. The main Bragg reflections of the powder diffraction pattern could be indexed in space group *P*6₃/*m* with similar lattice parameters to those of the published powder diffraction data (Kreidler & Hummel, 1970). Some broad and weak Bragg reflections were matched by the pattern of BaCO₃ in space group *Pm**cn*. The synchrotron X-ray wavelength was calibrated as 0.998043 Å with an external *NIST* 640c silicon standard reference material.

Initial lattice parameters for the two phases were refined using *CELREF* (Laugier & Bochu, 2003). The *P*6₃/*m* crystal structure of Ba₅(PO₄)₃(OH) (Chengjun *et al.*, 2005) was used as a starting model for the Rietveld (Rietveld, 1969) refinement of the structure of Ba₅(AsO₄)₃Cl. The crystal structure of witherite (de Villiers *et al.*, 1971) was used as a starting model for refinement of the structure of BaCO₃. Isotropic atomic displacement parameters were used for both phases. For the Ba₅(AsO₄)₃Cl phase the As—O distances in the AsO₄ tetrahedral units were constrained to those for mimetite (Dai *et al.*, 1991). For the BaCO₃ phase the C—O distances of the trigonal carbonate anion were constrained to those in witherite, and the U_{iso} factors for all atoms in the carbonate anion were constrained to be the same. As the Ba₅(AsO₄)₃Cl phase was prepared by ion-exchange of Pb₅(AsO₄)₃Cl, Rietveld refinements were done with the metal sites partially occupied by both Pb and Ba. However, this resulted in the refined Pb occupancies falling to zero. Therefore the occupancies of the metal sites were fixed as fully occupied by Ba and no Pb was included for the final refinement of the Ba₅(AsO₄)₃Cl phase. Proportions of the two phases were refined as 64.7 (9) wt.% Ba₅(AsO₄)₃Cl and 35.3 (9) wt.% BaCO₃.

Figures

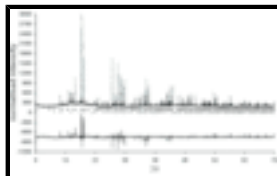


Fig. 1. Rietveld difference plot for the multi-phase refinement of Ba₅(AsO₄)₃Cl and BaCO₃. The black dots, and grey and black lines show respectively the observed, calculated and difference plots. Calculated Bragg reflection positions are indicated by triangles for the Ba₅(AsO₄)₃Cl phase and by crosses for the BaCO₃ phase.

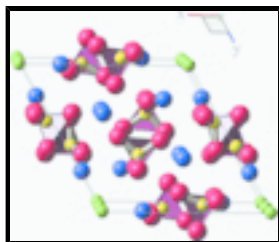


Fig. 2. The crystal structure of $\text{Ba}_5(\text{AsO}_4)_3\text{Cl}$. Pink tetrahedra show AsO_4 units with As^{5+} cations as yellow spheres and O^{2-} anions as red spheres. Large blue spheres represent Ba^{2+} cations and small green spheres Cl^- anions.

pentabarium tris(arsenate(V)) chloride

Crystal data

$\text{As}_3\text{Ba}_5\text{Cl}_1\text{O}_{12}$

$M_r = 1138.85$

Hexagonal, $P6_3/m$

$a = 10.5570 (1) \text{ \AA}$

$b = 10.5570 (1) \text{ \AA}$

$c = 7.73912 (8) \text{ \AA}$

$\alpha = 90^\circ$

$\beta = 90^\circ$

$\gamma = 120^\circ$

$V = 746.98 (1) \text{ \AA}^3$

$Z = 2$

$D_x = 5.063 (1) \text{ Mg m}^{-3}$

Synchrotron radiation

$\lambda = 0.998043 \text{ \AA}$

$\mu = 56.07 (1) \text{ mm}^{-1}$

$T = 298 \text{ K}$

Specimen shape: cylinder

$40 \times 0.7 \times 0.7 \text{ mm}$

Specimen prepared at 100 kPa

Specimen prepared at 1258 K

Particle morphology: powder, white

Data collection

In-house design
diffractometer

Monochromator: Si(111) channel-cut crystal

Specimen mounting: capillary

Specimen mounted in transmission mode

Scan method: step

$T = 298 \text{ K}$

$2\theta_{\min} = 2, 2\theta_{\max} = 70^\circ$

Increment in $2\theta = 0.01^\circ$

Increment in $2\theta = 0.01^\circ$

Refinement

$R_p = 0.059$

$R_{wp} = 0.082$

$R_{\text{exp}} = 0.067$

$R_B = 0.090$

$S = 1.23$

Wavelength of incident radiation: 0.998043 \AA

Excluded region(s): 2-6 degrees 2θ .

Profile function: Fundamental Parameters

21 parameters

3 constraints

?

$(\Delta/\sigma)_{\max} = 0.001$

Preferred orientation correction: None

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ba1	0.3333	0.6667	0.0061 (9)	0.059 (1)
Ba2	0.2445 (4)	0.9874 (6)	0.2500	0.065 (1)

supplementary materials

As1	0.4047 (7)	0.3716 (7)	0.2500	0.059 (2)
O1	0.347 (7)	0.495 (6)	0.2500	0.13 (2)
O2	0.591 (4)	0.473 (4)	0.2500	0.08 (1)
O3	0.354 (2)	0.280 (3)	0.068 (3)	0.065 (8)
Cl1	0.0000	0.0000	0.0000	0.070 (6)

Geometric parameters (Å, °)

Ba1—O1 ⁱ	2.67 (5)	Ba2—O3 ^{vi}	2.62 (4)
Ba1—O1 ⁱⁱ	2.67 (5)	Ba2—O3 ^{vii}	3.05 (4)
Ba1—O1	2.67 (5)	Ba2—O3 ^{viii}	3.05 (4)
Ba1—O2 ⁱⁱⁱ	2.81 (4)	Ba2—O1 ⁱⁱ	3.14 (4)
Ba1—O2 ^{iv}	2.81 (4)	Ba2—Cl1 ^{viii}	3.281 (5)
Ba1—O2 ^v	2.81 (4)	Ba2—Cl1 ^{ix}	3.281 (5)
Ba1—O3 ^{iv}	3.12 (3)	As1—O3	1.64 (2)
Ba1—O3 ⁱⁱⁱ	3.12 (3)	As1—O3 ^x	1.64 (2)
Ba1—O3 ^v	3.12 (3)	As1—O1	1.70 (8)
Ba2—O2 ⁱ	2.59 (4)	As1—O2	1.70 (4)
Ba2—O3 ^{iv}	2.62 (4)		
O3—As1—O3 ^x	118 (2)	O3—As1—O2	108 (2)
O3—As1—O1	108 (1)	O3 ^x —As1—O2	108 (2)
O3 ^x —As1—O1	108 (1)	O1—As1—O2	106 (2)

Symmetry codes: (i) $-y+1, x-y+1, z$; (ii) $-x+y, -x+1, z$; (iii) $x-y, x, -z$; (iv) $y, -x+y+1, -z$; (v) $-x+1, -y+1, -z$; (vi) $y, -x+y+1, z+1/2$; (vii) $x, y+1, -z+1/2$; (viii) $x, y+1, z$; (ix) $-x, -y+1, z+1/2$; (x) $x, y, -z+1/2$.

Fig. 1

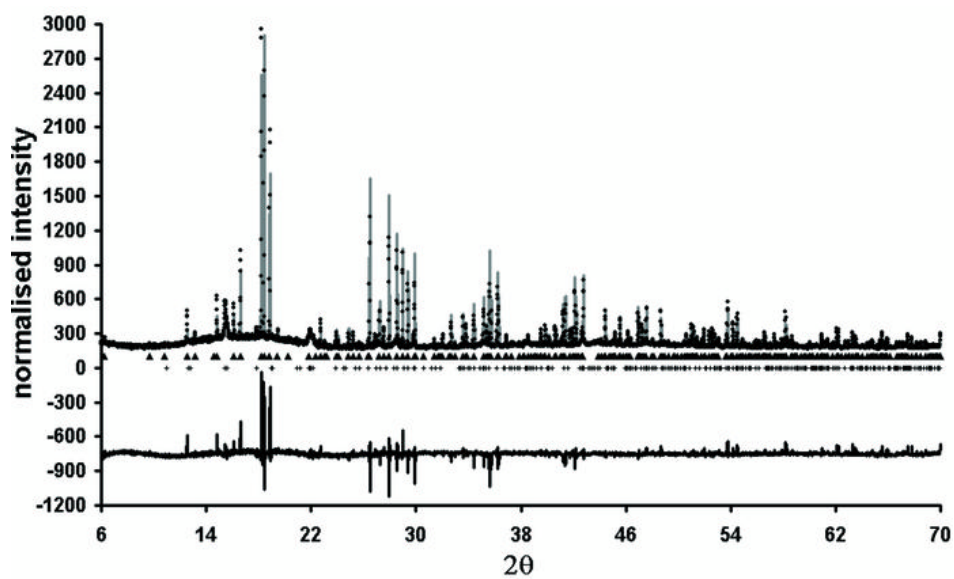


Fig. 2

