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Rietveld refinement of Ba$_5$(AsO$_4$)$_3$Cl from high-resolution synchrotron data

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Key indicators:
- powder synchrotron study; T = 298 K; mean σ(As–O) = 0.040 Å; R factor = 0.059; wR factor = 0.082; data-to-parameter ratio = 22.1.

The apatite-type compound Ba$_5$(AsO$_4$)$_3$Cl, pentabarium tris[arsenate(V)] chloride, has been synthesized by ion exchange at high temperature from a synthetic sample of mimetite (Pb$_5$(AsO$_4$)$_3$Cl) with BaCO$_3$ as a by-product. The exchange at high temperature from a synthetic sample of tris[arsenate(V)] chloride, has been synthesized by ion exchange at high temperature from a synthetic sample of mimetite (Pb$_5$(AsO$_4$)$_3$Cl) with BaCO$_3$ 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 space group $P6_3/m$. The structure consists of isolated tetrahedral AsO$_4^{3-}$ anions ($m$ symmetry), separated by two crystallographically independent Ba$^{2+}$ cations that are located on mirror planes and threefold rotation axes, respectively. The Cl$^{-}$ anions are at the 2h sites ($3$ 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-François et al. (1979). For synthetic work, see: Baker (1966); Essington (1988); Harrison et al. (2002).

Table 1

|                  | Ba$^+$ 1 | Ba$^+$ 2 | Ba$^+$ 3 | O$^-$ 1  | O$^-$ 2  | O$^-$ 3  |
|------------------|----------|----------|----------|----------|----------|----------|
| O$^-$ 1–O$^-$ 2  | 2.67 (5) | 2.81 (4) | 3.12 (3) | 3.12 (3) | 3.12 (3) | 3.14 (4) |
| O$^-$ 1–O$^-$ 3  | 2.59 (4) | 2.62 (4) | 2.62 (4) | 2.62 (4) | 2.62 (4) | 2.62 (4) |
| O$^-$ 2–O$^-$ 3  | 3.05 (4) | 3.05 (4) | 3.05 (4) | 3.05 (4) | 3.05 (4) | 3.05 (4) |

Symmetry codes: (i) $x$, $y$, $-z$; (ii) $-y$, $x$, $-z$; (iii) $y$, $-x$, $y$; (iv) $-x$, $y$, $z$; (v) $x$, $y$, $z$; (vi) $x$, $y$, $-z$.

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: pubCIF (Westrip, 2008).

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

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supplementary materials
Rietveld refinement of Ba$_5$(AsO$_4$)$_3$Cl from high-resolution synchrotron data

A. M. T. Bell, C. M. B. Henderson, R. F. Wendlandt and W. J. Harrison

Comment

Apatites are minerals and synthetic compounds with general formula $A_5(PO_4)_3X$, 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 Ba$_5$(AsO$_4$)$_3$Cl (Kreidler & Hummel, 1970) and for (Ba$_{2.25}$Ca$_{1.65}$Fe$_{0.06}$Mg$_{0.06}$)$_2$[(AsO$_4$)$_{2.56}$PO$_4$]O$_{3}$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 Ba$_5$(AsO$_4$)$_2$SO$_4$S (Schiff-Francois et al., 1979) and (Sr$_{1.66}$Ba$_{0.34}$)(Ba$_{2.61}$Sr$_{0.39}$)(AsO$_4$)$_3$Cl (Dordevic et al., 2008). The crystal structure of Ba$_5$(AsO$_4$)$_3$Cl in space group $P6_3/m$ is reported in the present communication.

Table 1 shows refined interatomic distances and angles for the Ba$_5$(AsO$_4$)$_3$Cl 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 Ba$_5$(VO$_4$)$_3$Cl (Roh & Hong, 2005), 2.83 Å and 2.79 Å for Ba$_5$(PO$_4$)$_3$Cl (Hata et al., 1979) and 2.83 Å and 2.76 Å for Ba$_5$(MnO$_4$)$_3$Cl (Reinen et al., 1986). The As—O distances are characteristic for tetrahedral AsO$_4^{3-}$ 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 Ba$_5$(AsO$_4$)$_3$Cl 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 Ba$_5$(AsO$_4$)$_3$Cl 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 Ba$_5$(AsO$_4$)$_3$Cl, showing the isolated tetrahedral AsO$_4^{3-}$ anions separated by Ba$^{2+}$ cations and Cl$^-$ anions, is displayed in Fig. 2.

Experimental

This work was part of an attempt to synthesize analogues of Pb$_5$(AsO$_4$)$_3$Cl (mimetite) with Pb$^{2+}$ substituted by alkaline earth cations. All starting materials were well crystallized solids. Pb$_5$(AsO$_4$)$_3$Cl was precipitated by titration of 0.1M Na$_2$HASO$_4$ into a well stirred, saturated PbCl$_2$ solution at room temperature (procedure modified from methods of Baker (1966) and
supplementary materials

Essington (1988)). The molar ratio of Pb:As was slightly greater than 5:3, allowing for excess PbCl$_2$ 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 reduced the conductivity of the wash water to $< 50 \mu S \text{cm}^{-1}$. Ba$_5$(AsO$_4$)$_3$Cl was successfully synthesized by ion exchange of Pb$_5$(AsO$_4$)$_3$Cl with molten BaCl$_2$ 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 BaCl$_2$ was removed from the solids by repeated washing with de-ionized water followed by centri fugation 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 $P6_3/m$ 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 BaCO$_3$ in space group $Pmcn$. The synchrotron X-ray wavelength was calibrated as 0.998043Å with an external NIST 640c silicon standard reference material.

Initial lattice parameters for the two phases were refined using CELREF (Laugier & Bochu, 2003). The $P6_3/m$ crystal structure of Ba$_5$(PO$_4$)$_3$(OH) (Chengjun et al., 2005) was used as a starting model for the Rietveld (Rietveld, 1969) refinement of the structure of Ba$_5$(AsO$_4$)$_3$Cl. The crystal structure of witherite (de Villiers et al., 1971) was used as a starting model for refinement of the structure of BaCO$_3$. Isotropic atomic displacement parameters were used for both phases. For the Ba$_5$(AsO$_4$)$_3$Cl phase the As—O distances in the AsO$_4$ tetrahedral units were constrained to those for mimetite (Dai et al., 1991). For the BaCO$_3$ 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 Ba$_5$(AsO$_4$)$_3$Cl phase was prepared by ion-exchange of Pb$_5$(AsO$_4$)$_3$Cl, 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 Ba$_5$(AsO$_4$)$_3$Cl phase. Proportions of the two phases were refined as 64.7 (9) wt.% Ba$_5$(AsO$_4$)$_3$Cl and 35.3 (9) wt.% BaCO$_3$.

Figures

Fig. 1. Rietveld difference plot for the multi-phase refinement of Ba$_5$(AsO$_4$)$_3$Cl and BaCO$_3$. 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 Ba$_5$(AsO$_4$)$_3$Cl phase and by crosses for the BaCO$_3$ phase.
Fig. 2. The crystal structure of Ba$_5$(AsO$_4$)$_3$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.

pentabarum tris(arsenate(V)) chloride

Crystal data

As$_3$Ba$_5$Cl$_1$O$_{12}$  
$M_r = 1138.85$  
Hexagonal, $P6_3/m$  
a = 10.5570 (1) Å  
b = 10.5570 (1) Å  
c = 7.73912 (8) Å  
$\alpha = 90^\circ$  
$\beta = 90^\circ$  
$\gamma = 120^\circ$  
$V = 746.98$ (1) Å$^3$

Z = 2  
$D_x = 5.063$ (1) Mg m$^{-3}$  
Synchrotron radiation  
$\lambda = 0.998043$ Å  
$\mu = 56.07$ (1) mm$^{-1}$  
$T = 298$ K  
Specimen shape: cylinder  
40 × 0.7 × 0.7 mm  
Specimen prepared at 100 kPa  
Specimen prepared at 1258 K  
Particle morphology: powder, white

Data collection

In-house design diffractometer  
$T = 298$ K  
Monochromator: Si(111) channel-cut crystal  
$2\theta_{\text{min}} = 2$, $2\theta_{\text{max}} = 70^\circ$  
Specimen mounting: capillary  
Increment in $2\theta = 0.01^\circ$  
Specimen mounted in transmission mode  
Increment in $2\theta = 0.01^\circ$  
Scan method: step

Refinement

$R_p = 0.059$  
$R_{wp} = 0.082$  
$R_{exp} = 0.067$  
$R_B = 0.090$  
$S = 1.23$  
Profile function: Fundamental Parameters  
Wavelength of incident radiation: 0.998043 Å  
Preferred orientation correction: None

$R_p$ = 0.059  
$R_{wp}$ = 0.082  
$R_{exp}$ = 0.067  
$R_B$ = 0.090  
$S$ = 1.23  
Profile function: Fundamental Parameters

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)

|     | x    | y    | z    | $U_{iso}$ $/ U_{eq}$ |
|-----|------|------|------|----------------------|
| 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

|        | x     | y     | z     | U(eq)  |
|--------|-------|-------|-------|--------|
| 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 | 2.67 (5) | Ba2—O3  | 2.62 (4) |
| Ba1—O1' | 2.67 (5) | Ba2—O3' | 3.05 (4) |
| Ba2—O3  | 3.05 (4) |
| Ba1—O2  | 2.81 (4) | Ba2—O1' | 3.14 (4) |
| Ba1—O2' | 2.81 (4) | Ba2—O1  | 3.281 (5) |
| Ba1—O2'' | 2.81 (4) | Ba2—Cl1 | 3.281 (5) |
| Ba1—O3  | 3.12 (3) | As1—O3  | 1.64 (2) |
| Ba1—O3' | 3.12 (3) | As1—O3' | 1.64 (2) |
| Ba1—O3'' | 3.12 (3) | As1—O1  | 1.70 (8) |
| Ba2—O2  | 2.59 (4) | As1—O2  | 1.70 (4) |
| Ba2—O3  | 2.62 (4) |
| O3—As1—O3 | 118 (2) | O3—As1—O2 | 108 (2) |
| O3—As1—O1 | 108 (1) | O3—As1—O2 | 108 (2) |
| O3—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