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

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

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Synchrotron Radiation Source, STFC Daresbury Laboratory, Daresbury, Warrington, Cheshire, WA4 4AD, England, a School of Earth, Atmospheric and Environmental Sciences, University of Manchester, Manchester, M13 9PL, England, and b Department of Geology and Geological Engineering, Colorado School of Mines, Golden, CO 80401, USA

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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$_4$(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 structure as other halogenoapatites with general formula $A_x$(YO$_4$)$_3$X ($A =$ divalent cation, $Y =$ pentavalent cation, $X =$ Cl, Br) in space group $P6_3/m$. The structure consists of isolated tetrahedral AsO$_4$- 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 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: Dordevic 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).

Data collection

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

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

Table 1

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<tr>
<td>$S$</td>
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</tr>
<tr>
<td>Excluded region(s); 2-6 degrees 2$	heta$</td>
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</tbody>
</table>

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).

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.

References

inorganic compounds

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 $A_5(YO_4)_3X$, 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 Ba$_5$(AsO$_4$)$_3$Cl (Kreidler & Hummel, 1970) and for (Ba$_{2.25}$Ca$_{1.65}$Pb$_{1.16}$Fe$_{0.06}$Mg$_{0.06}$)[(AsO$_4$)$_{2.56}$(PO$_4$)$_{0.3}$]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 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 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 reduced 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 P6₃/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 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 P6₃/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 Uiso 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 Ba₅(AsO₄)₃Cl. Pink tetrahedra show AsO₄ units with As⁵⁺ cations as yellow spheres and O²⁻ anions as red spheres. Large blue spheres represent Ba²⁺ cations and small green spheres Cl⁻ anions.

pentabarium tris(arsenate(V)) chloride

Crystal data

As₅Ba₅Cl₁O₁₂, Z = 2
Mr = 1138.85
Hexagonal, P6₃/m
a = 10.5570 (1) Å
b = 10.5570 (1) Å
c = 7.73912 (8) Å
α = 90°
β = 90°
γ = 120°
V = 746.98 (1) Å³

Data collection

In-house design diffractometer
Monochromator: Si(111) channel-cut crystal
2θ min = 2, 2θ max = 70°
Specimen mounted in transmission mode
Increment in 2θ = 0.01°
Scan method: step

Refinement

Rp = 0.059
Rwp = 0.082
Rexp = 0.067
R_B = 0.090
S = 1.23
Wavelength of incident radiation: 0.998043 Å
Excluded region(s): 2-6 degrees 2θ.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

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supplementary materials

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**Geometric parameters (Å, °)**

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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