Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Rietveld refinement of $Sr_5(AsO_4)_3Cl$ from high-resolution synchrotron data

Anthony M. T. Bell,[a]* C. Michael B. Henderson,[b] Richard F. Wendlandt[c] and Wendy J. Harrison[c]

[a]Synchrotron Radiation Source, STFC Daresbury Laboratory, Daresbury, Warrington, Cheshire WA4 4AD, England, [b]School of Earth, Atmospheric and Environmental Sciences, University of Manchester, Manchester, M13 9PL, England, and [c]Department of Geology and Geological Engineering, Colorado School of Mines, Golden, CO 80401, USA
Correspondence e-mail: ynotlleb1@mac.com

Received 6 February 2009; accepted 11 February 2009

Key indicators: powder synchrotron study; T = 298 K; mean σ(As–O) = 0.020 Å; R factor = 0.052; wR factor = 0.066; data-to-parameter ratio = 14.1.

The apatite-type compound, pentastrontium tris[arsenate(V)] chloride, $Sr_5(AsO_4)_3Cl$, has been synthesized by ion exchange at high temperature from a synthetic sample of mimetite [$Pb_5(AsO_4)_3Cl$] with $SrCO_3$ 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 $A_5(YO_4)_3X$ (A = divalent cation, Y = pentavalent cation, and X = F, Cl or Br) in the space group $P6_3/m$. The structure consists of isolated tetrahedral AsO_4^{3-} anions (the As atom and two O atoms have m symmetry), separated by two crystallographically independent Sr^{2+} cations that are located on mirror planes and threefold rotation axes, respectively. One Sr atom is coordinated by nine O atoms and the other by six. The chloride anions (site symmetry $\overline{3}$) are at the 2a sites 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 Sr As-apatite, see: Kreidler & Hummel (1970). Atomic coordinates as starting parameters for the Rietveld (Rietveld, 1969) refinement of the present phases were taken from Bell *et al.* (2008); Dai *et al.* (1991); de Villiers *et al.* (1971). For related Sr—Cl-apatites, see: Đordević *et al.* (2008); Sudarsanan & Young, (1974, 1980); Beck *et al.* (2006); Noetzold *et al.* (1995); Noetzold & Wulff (1996, 1997, 1998); Swafford & Holt (2002); Wardojo & Hwu (1996). For synthetic work, see: Baker (1966); Essington (1988); Harrison *et al.* (2002).

Experimental

Crystal data

$Sr_5(AsO_4)_3Cl$
M_r = 890.31
Hexagonal, $P6_3/m$
a = 10.1969 (1) Å
c = 7.28108 (9) Å
V = 655.63 (2) Å^3
Z = 2
Synchrotron radiation
λ = 0.998043 Å
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
Specimen mounting: capillary
Specimen mounted in transmission mode
Scan method: step
Absorption correction: fixed at 0
$2\theta_{min}$ = 2, $2\theta_{max}$ = 60°
Increment in 2θ = 0.01°

Refinement

R_p = 0.052
R_{wp} = 0.066
R_{exp} = 0.047
R_B = 0.090
S = 2.00
Excluded region(s): 2-6° 2θ
Profile function: Pseudo Voigt
225 reflections
16 parameters
Preferred orientation correction: none

Table 1
Selected geometric parameters (Å, °).

Sr1—O1	2.49 (2)	Sr2—O1^{v}	3.02 (2)
Sr1—O2^{i}	2.59 (2)	Sr2—Cl1^{iv}	3.156 (3)
Sr1—O3^{i}	3.01 (1)	As1—O3	1.57 (1)
Sr2—O2^{ii}	2.53 (2)	As1—O1	1.72 (2)
Sr2—O3^{iii}	2.44 (1)	As1—O2	1.70 (2)
Sr2—O3^{iv}	2.94 (1)		
O3—As1—O3^{vi}	121 (1)	O3—As1—O2	106.3 (6)
O3—As1—O1	105.8 (7)	O1—As1—O2	112 (1)

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) and *GSAS* (Larson & Von Dreele (2004); data reduction: local software; method used to solve structure: coordinates taken from a related compound; program(s) used to refine structure: *GSAS* and *EXPGUI* (Toby, 2001); molecular graphics: *VESTA* (Momma & Izumi, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2009).

AMTB acknowledges the use of the EPSRC's Chemical Database Service at Daresbury (Fletcher *et al.*, 1996).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2096).

References

Baker, W. E. (1966). *Am. Mineral.* **51**, 1712–1721.
Beck, H. P., Douiheche, M., Haberkorn, R. & Kohlmann, H. (2006). *Solid State Sci.* **8**, 64–70.
Bell, A. M. T., Henderson, C. M. B., Wendlandt, R. F. & Harrison, W. J. (2008). *Acta Cryst.* E**64**, i63–i64.
Dai, Y.-S., Hughes, J. M. & Moore, P. B. (1991). *Can. Mineral.* **29**, 369–376.
Đordević, T., Šutović, S., Stojanović, J. & Karanović, Lj. (2008). *Acta Cryst.* C**64**, i82–i86.
Essington, M. E. (1988). *Soil Sci. Soc. Am. J.* **52**, 1566–1570.
Fletcher, D. A., McMeeking, R. F. & Parkin, D. J. (1996). *Chem. Inf. Comput. Sci.* **36**, 746–749.

Harrison, W. J., Wendlandt, R. F. & Wendlandt, A. E. (2002). International Mineralogical Association 18th General Meeting, Sept 1–6, 2002, Edinburgh, Scotland. Abstract A18–10, meeting program with abstracts, page 185.
Kreidler, E. R. & Hummel, F. A. (1970). *Am. Mineral.* **55**, 170–184.
Larson, A. C. & Von Dreele, R. B. (2004). General Structure Analysis System (*GSAS*). Report LAUR 86-748. Los Alamos National Laboratory, New Mexico, USA.
Laugier, J. & Bochu, B. (2003). *CELREF*. http://www.*CCP14*.ac.uk/tutorial/lmgp/*CELREF*.htm.
Mercier, P. H. J., Le Page, Y., Whitfield, P. S., Mitchell, L. D., Davidson, I. J. & White, T. J. (2005). *Acta Cryst.* B**61**, 635–655.
Momma, K. & Izumi, F. (2008). *J. Appl. Cryst.* **41**, 653–658.
Noetzold, D. & Wulff, H. (1996). *Phys. Status Solidi Sect. A*, **158** 303–311.
Noetzold, D. & Wulff, H. (1997). *Phys. Status Solidi Sect. A*, **160** 227–236.
Noetzold, D. & Wulff, H. (1998). *Phys. Status Solidi Sect. B*, **207** 271–281.
Noetzold, D., Wulff, H. & Herzog, G. (1995). *Phys. Status Solidi Sect. B*, **191** 21–30.
Rietveld, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.
Sudarsanan, K. & Young, R. A. (1974). *Acta Cryst.* B**30**, 1381–1386.
Sudarsanan, K. & Young, R. A. (1980). *Acta Cryst.* B**36**, 1525–1530.
Swafford, S. H. & Holt, E. M. (2002). *Solid State Sci.* **4**, 807–812.
Toby, B. H. (2001). *J. Appl. Cryst.* **34**, 210–213.
Villiers, J. P. R. de (1971). *Am. Mineral.* **56**, 758–766.
Wardojo, T. A. & Hwu, S.-J. (1996). *Acta Cryst.* C**52**, 2959–2960.
Westrip, S. P. (2009). *publCIF*. In preparation.
White, T. J. & ZhiLi, D. (2003). *Acta Cryst.* B**59**, 1–16.
Wu, P., Zeng, Y. Z. & Wang, C. M. (2003). *Biomaterials*, **25**, 1123–1130.

supporting information

Acta Cryst. (2009). E**65**, i16–i17 [doi:10.1107/S1600536809005054]

Rietveld refinement of $Sr_5(AsO_4)_3Cl$ from high-resolution synchrotron data

Anthony M. T. Bell, C. Michael B. Henderson, Richard F. Wendlandt and Wendy J. Harrison

S1. 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), White & ZhiLi (2003) and Wu *et al.*, (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 Sr containing As-apatite $Sr_5(AsO_4)_3Cl$ (Kreidler & Hummel, 1970) was indexed in space group $P6_3/m$. Related crystal structures have also been reported for $Ca_5(AsO_4)_3Cl$ (Wardojo and Hwu, 1996) and for $Sr_5(AsO_4)_3F$ and $(Sr_{1.66}Ba_{0.34})(Ba_{2.61}Sr_{0.39})(AsO_4)_3Cl$ (Đordević *et al.*, 2008). The crystal structure of $Sr_5(AsO_4)_3Cl$ in space group $P6_3/m$ is reported in the present communication. We recently reported the related crystal structure of $Ba_5(AsO_4)_3Cl$ (Bell *et al.*, 2008).

Table 1 shows refined interatomic distances and angles for the $Sr_5(AsO_4)_3Cl$ structure. The averaged Sr1—O and Sr2—O distances of respectively 2.70 Å and 2.72 Å, compare with Sr1—O and Sr2—O distances in: $Sr_5(AsO_4)_3F$ (Đordević *et al.* 2008) of 2.71 Å and 2.62 Å; 2.71 Å and 2.63 Å for $Sr_5(VO_4)_3Cl$ (Beck *et al.*, 2006); 2.67 Å and 2.62 Å for $Sr_5(PO_4)_3Cl$ (Sudarsanan and Young, 1974); and 2.67 Å and 2.59 Å for $Sr_5(PO_4)_3F$ (Swafford and Holt, 2002). The As—O distances are characteristic for tetrahedral AsO_4 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 $Sr_5(AsO_4)_3Cl$ are similar to the previously published parameters of a = 10.18 Å, c = 7.28 Å given by Kreidler & Hummel (1970). Fig. 1 shows the Rietveld difference plot for the present refinement. The crystal structure of $Sr_5(AsO_4)_3Cl$, showing the isolated tetrahedral AsO_4^{3-} anions separated by Sr^{2+} cations and Cl^- anions, is displayed in Fig. 2.

S2. Experimental

This work was part of an attempt to synthesize analogues of $Pb_5(AsO_4)_3Cl$ (mimetite) with Pb^{2+} substituted by alkaline earth cations. All starting materials were well crystallized solids. $Pb_5(AsO_4)_3Cl$ was precipitated by titration of 0.1*M* Na_2HAsO_4 into a well stirred, saturated $PbCl_2$ solution at room temperature (procedure modified from methods of Baker (1966) and 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 reduce the conductivity of the wash water to < 50 $\mu S{\cdot}cm^{-1}$. $Sr_5(AsO_4)_3Cl$ was successfully synthesized by ion exchange of $Pb_5(AsO_4)_3Cl$ with molten $SrCl_2$ 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 $SrCl_2$ was removed from the solids by repeated washing with de-ionized water followed by centrifugation and filtration to separate the solid from the solution.

S3. Refinement

The main Bragg reflections of the high resolution synchrotron X-ray powder diffraction pattern could be indexed in space group *P*6_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 $SrCO_3$ in space group *Pmcn*.

Initial lattice parameters for the two phases were refined using *CELREF* (Laugier & Bochu, 2003). The *P*6_3/*m* crystal structure of $Ba_5(AsO_4)_3Cl$ (Bell *et al.*, 2008) was used as a starting model for the Rietveld (Rietveld, 1969) refinement of the structure of $Sr_5(AsO_4)_3Cl$. The crystal structure of strontianite (de Villiers *et al.*, 1971) was used as a starting model for refinement of the structure of $SrCO_3$. Isotropic atomic displacement parameters were used for both phases. For the $Sr_5(AsO_4)_3Cl$ phase soft constraints were used for the As—O distances in the AsO_4 tetrahedral units. These distances were restrained to those for mimetite (Dai *et al.*, 1991). For the $SrCO_3$ phase only the coordinates and the atomic displacement parameters for Sr were refined, the C and O coordinates were fixed to those in the starting model and the C and O atomic displacement parameters were fixed at zero. Proportions of the two phases were refined as 76.6 (1) wt.% $Sr_5(AsO_4)_3Cl$ and 23.4 (1) wt.% $SrCO_3$.

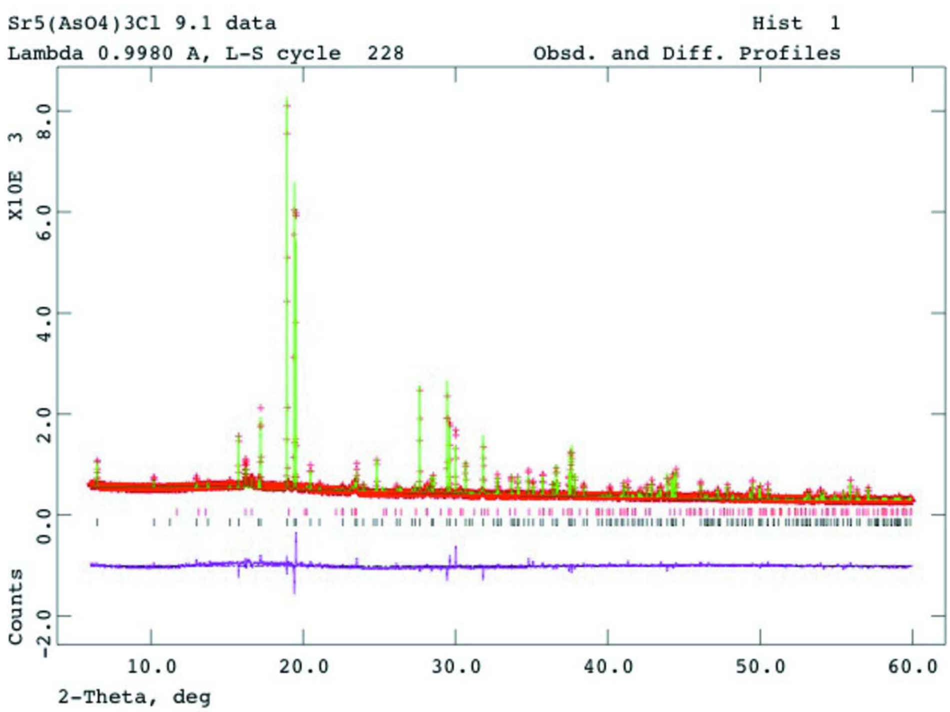

Figure 1

Rietveld difference plot for the multi-phase refinement of $Sr_5(AsO_4)_3Cl$ and $SrCO_3$. The red crosses, and green and pink lines show respectively the observed, calculated and difference plots. Calculated Bragg reflection positions are indicated by black lines for the $Sr_5(AsO_4)_3Cl$ phase and by red lines for the $SrCO_3$ phase.

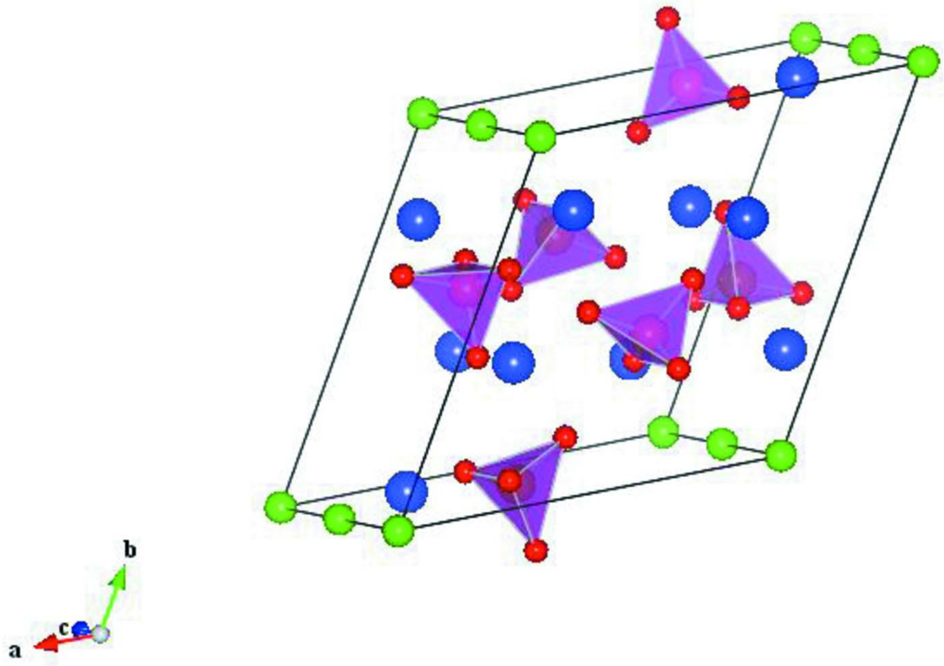

Figure 2

The crystal structure of $Sr_5(AsO_4)_3Cl$. Pink tetrahedra show AsO_4 units with As^{5+} cations as orange spheres and O^{2-} anions as red spheres. Large blue spheres represent Sr^{2+} cations and small green spheres Cl^- anions.

pentastrontium tris[arsenate(V)] chloride

Crystal data

$Sr_5(AsO_4)_3Cl$
M_r = 890.31
Hexagonal, $P6_3/m$
a = 10.1969 (1) Å
c = 7.28108 (9) Å
V = 655.63 (2) Å^3
Z = 2
D_x = 4.510 (1) Mg m^{-3}
Synchrotron radiation, λ = 0.998043 Å
T = 298 K
Particle morphology: powder
white
cylinder, 40 × 0.7 mm
Specimen preparation: Prepared at 1258 K and 100 kPa

Data collection

In-house design diffractometer
Radiation source: Synchrotron
Si(111) channel-cut crystal monochromator
Specimen mounting: capillary
Data collection mode: transmission
Scan method: step
$2\theta_{min}$ = 6°, $2\theta_{max}$ = 60°, $2\theta_{step}$ = 0.01°

Refinement

R_p = 0.052
R_{wp} = 0.066
R_{exp} = 0.047
R_{Bragg} = 0.090
$R(F^2)$ = 0.33148
χ^2 = 3.992
5801 data points
Excluded region(s): 2-6° 2θ
Profile function: Pseudo Voigt
16 parameters
0 restraints
4 constraints
$(\Delta/\sigma)_{max}$ = 0.001
Background function: Cosine Fourier Series
Preferred orientation correction: None

Special details

Experimental. Absorption correction fixed at zero, all attempts to refine this term in GSAS were unsuccessful so this term was fixed at zero. CELREF was used for initial lattice parameter determinations before Rietveld refinement. Lattice parameters from GSAS refinement are quoted in the paper.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Sr1	0.33333	0.66667	0.008 (1)	0.0246 (9)
Sr2	0.2496 (5)	0.9936 (6)	0.25	0.0246 (9)
As1	0.4057 (5)	0.3718 (5)	0.25	0.029 (2)
O1	0.337 (3)	0.496 (2)	0.25	0.015 (4)
O2	0.598 (2)	0.464 (2)	0.25	0.015 (4)
O3	0.354 (2)	0.284 (2)	0.063 (2)	0.015 (4)
Cl1	0.0000	0.0000	0.0000	0.031 (5)

Geometric parameters (Å, º)

Sr1—O1^{i}	2.49 (2)	Sr2—O3^{vi}	2.44 (1)
Sr1—O1^{ii}	2.49 (2)	Sr2—O3^{vii}	2.94 (1)
Sr1—O1	2.49 (2)	Sr2—O3^{viii}	2.94 (1)
Sr1—O2^{iii}	2.59 (2)	Sr2—O1^{ii}	3.02 (2)
Sr1—O2^{iv}	2.59 (2)	Sr2—Cl1^{viii}	3.156 (3)
Sr1—O2^{v}	2.59 (2)	Sr2—Cl1^{ix}	3.156 (3)
Sr1—O3^{iv}	3.01 (1)	As1—O3	1.57 (1)
Sr1—O3^{iii}	3.01 (1)	As1—O3^{x}	1.57 (1)
Sr1—O3^{v}	3.01 (1)	As1—O1	1.72 (2)
Sr2—O2^{i}	2.53 (2)	As1—O2	1.70 (2)
Sr2—O3^{iv}	2.44 (1)		
O3—As1—O3^{x}	121 (1)	O3—As1—O2	106.3 (6)
O3—As1—O1	105.8 (7)	O3^{x}—As1—O2	106.3 (6)
O3^{x}—As1—O1	105.8 (7)	O1—As1—O2	112 (1)

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) $x, y, -z+1/2$.