inorganic compounds

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

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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 $\bar{3}$) 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: Đorđević *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

$Sr_5(AsO_4)_3Cl$	λ = 0.998043 Å
M_r = 890.31	T = 298 K
Hexagonal, $P6_3/m$	Specimen shape: cylinder
a = 10.1969 (1) Å	$40 \times 0.7 \times 0.7$ mm
c = 7.28108 (9) Å	Specimen prepared at 100 kPa
V = 655.63 (2) Å^3	Specimen prepared at 1258 K
Z = 2	Particle morphology: powder, white
Synchrotron radiation	

Data collection

In-house design diffractometer	Scan method: step
Specimen mounting: capillary	Absorption correction: fixed at 0
Specimen mounted in transmission mode	$2\theta_{min}$ = 2, $2\theta_{max}$ = 60°
	Increment in 2θ = 0.01°

Refinement

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

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).

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

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supplementary materials

Rietveld refinement of Sr$_5$(AsO$_4$)$_3$Cl 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), 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$_4$)$_3$Cl (Kreidler & Hummel, 1970) was indexed in space group $P6_3/m$. Related crystal structures have also been reported for Ca$_5$(AsO$_4$)$_3$Cl (Wardojo and Hwu, 1996) and for Sr$_5$(AsO$_4$)$_3$F and (Sr$_{1.66}$Ba$_{0.34}$)(Ba$_{2.61}$Sr$_{0.39}$)(AsO$_4$)$_3$Cl (Đordević *et al.*, 2008). The crystal structure of Sr$_5$(AsO$_4$)$_3$Cl in space group $P6_3/m$ is reported in the present communication. We recently reported the related crystal structure of Ba$_5$(AsO$_4$)$_3$Cl (Bell *et al.*, 2008).

Table 1 shows refined interatomic distances and angles for the Sr$_5$(AsO$_4$)$_3$Cl 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$_4$)$_3$F (Đordević *et al.* 2008) of 2.71 Å and 2.62 Å; 2.71 Å and 2.63 Å for Sr$_5$(VO$_4$)$_3$Cl (Beck *et al.*, 2006); 2.67 Å and 2.62 Å for Sr$_5$(PO$_4$)$_3$Cl (Sudarsanan and Young, 1974); and 2.67 Å and 2.59 Å for Sr$_5$(PO$_4$)$_3$F (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$_4$)$_3$Cl 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$_4$)$_3$Cl, showing the isolated tetrahedral AsO$_4{}^{3-}$ anions separated by Sr^{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 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 μS·cm^{-1}. Sr$_5$(AsO$_4$)$_3$Cl was successfully synthesized by ion exchange of Pb$_5$(AsO$_4$)$_3$Cl 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

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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.

Refinement

The main Bragg reflections of the high resolution synchrotron X-ray 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 $SrCO_3$ in space group *Pmcn*.

Initial lattice parameters for the two phases were refined using *CELREF* (Laugier & Bochu, 2003). The $P6_3/m$ 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.% $SrCO_3$.

Figures

Fig. 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.
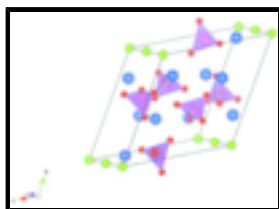

Fig. 2. The crystal structure of $Sr_5(AsO_4)_3Cl$. Pink tetrahedra show AsO_4 units with As^{5+} cations as orange spheres and O^{2-} anions as red spheres. Large blue spheres represent Sr^{2+} cations and small green spheres Cl^- anions.

pentastrontium tris[arsenate(V)] chloride

Crystal data

$Sr_5(AsO_4)_3Cl$	$Z = 2$
$M_r = 890.31$	$D_x = 4.510\ (1)\ \mathrm{Mg\ m^{-3}}$
Hexagonal, $P6_3/m$	Synchrotron radiation $\lambda = 0.998043$ Å
$a = 10.1969\ (1)$ Å	$T = 298$ K
$b = 10.1969\ (1)$ Å	Specimen shape: cylinder
$c = 7.28108\ (9)$ Å	$40 \times 0.7 \times 0.7$ mm

$\alpha = 90°$

$\beta = 90°$

$\gamma = 120°$

$V = 655.63 \,(2) \; \text{Å}^3$

Specimen prepared at 100 kPa

Specimen prepared at 1258 K

Particle morphology: powder, white

Data collection

In-house design diffractometer	Scan method: step
Monochromator: Si(111) channel-cut crystal	$T = 298$ K
Specimen mounting: capillary	$2\theta_{min} = 2$, $2\theta_{max} = 60°$
Specimen mounted in transmission mode	Increment in $2\theta = 0.01°$

Refinement

$R_p = 0.052$	Profile function: Pseudo Voigt
$R_{wp} = 0.066$	16 parameters
$R_{exp} = 0.047$	4 constraints
$R_B = 0.090$	?
$S = 2.00$	$(\Delta/\sigma)_{max} = 0.001$
Wavelength of incident radiation: 0.998043 Å	Preferred orientation correction: None
Excluded region(s): 2-6° 2θ	

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 (Å^2)

	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, °)

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, $-z+1/2$.

Fig. 1

Fig. 2