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Rietveld refinement of Sr$_5$(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) = 0.020 Å; R factor = 0.052; wR factor = 0.066; data-to-parameter ratio = 14.1.

The apatite-type compound, pentastrentonium tris[arsenate(V)] chloride, Sr$_5$(AsO$_4$)$_3$Cl, has been synthesized by ion exchange [Pb$_5$(AsO$_4$)$_3$Cl] 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$_6$(YO$_4$)$_5$X (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 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: Dordevic et al. (2008); Sudarsanan & Young, (1974, 1980); Beck et al. (2006); Noetzel et al. (1995); Noetzel & Wulf (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$_4$)$_3$Cl

$M_r$ = 890.31
Hexagonal, P6$_3$/m

$\alpha$ = 10.1969 (1) Å
$c$ = 7.28108 (9) Å
$V$ = 655.63 (2) Å$^3$
$Z$ = 2

Synchrotron radiation

Data collection

In-house design diffractometer

Specimen mounting: capillary

Specimen mounted in transmission mode

Scan method: step
Absorption correction: fixed at 0
$\theta$ min = 2, $\theta$ max = 60°
Increment in $\theta$ = 0.01°

Refinement

$R_p$ = 0.052
$R_p/w$ = 0.066
$R_w$ = 0.047
$S$ = 2.00

Profile function: Pseudo Voigt

16 parameters
Preferred orientation correction: none

Table 1

Selected geometric parameters (Å, °).

<table>
<thead>
<tr>
<th>Symmetry codes</th>
<th>Sr1—O1</th>
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<th>Sr2—O1$^*$</th>
<th>3.02 (2)</th>
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<td>Sr2—Cl1$^{4b}$</td>
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<td>As1—O3</td>
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<td>As1—O1</td>
<td>1.72 (2)</td>
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<tr>
<td>(iv)</td>
<td>Sr2—O2</td>
<td>2.44 (1)</td>
<td>As1—O2</td>
<td>1.70 (2)</td>
</tr>
<tr>
<td>(v)</td>
<td>Sr2—O2</td>
<td>2.94 (1)</td>
<td>O3—As1—O3$^{4b}$</td>
<td>121 (1)</td>
</tr>
<tr>
<td>(vi)</td>
<td>O3—As1—O3$^{4b}$</td>
<td>105.8 (7)</td>
<td>O1—As1—O2</td>
<td>112 (1)</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) x + y, y, z; (ii) −y + 1, x + y + z; (iii) y, −x + y + 1, −z; (iv) x, y + z, z; (v) −x + y, −x + z, z; (vi) x, y, −z + 1

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: publICIF (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


supplementary materials
Rietveld refinement of Sr$_5$(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), 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 (&Dstroko;ordević 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 (Dstroko;ordević 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 $<50$ µScm$^{-1}$. 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
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\(_4\))\(_3\)Cl (Bell et al., 2008) was used as a starting model for the Rietveld (Rietveld, 1969) refinement of the structure of Sr\(_5\)(AsO\(_4\))\(_3\)Cl. 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\(_4\))\(_3\)Cl 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\(_4\))\(_3\)Cl and 23.4 (1) wt.% SrCO\(_3\).

**Figures**

Fig. 1. Rietveld difference plot for the multi-phase refinement of Sr\(_5\)(AsO\(_4\))\(_3\)Cl 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\(_4\))\(_3\)Cl phase and by red lines for the SrCO\(_3\) phase.

Fig. 2. The crystal structure of Sr\(_5\)(AsO\(_4\))\(_3\)Cl. 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**

\[
\begin{align*}
\text{Sr}_5(\text{AsO}_4)_3\text{Cl} & \quad Z = 2 \\
M_r &= 890.31 \\
\text{Hexagonal, } P6_3/m & \\
ap &= 10.1969 (1) \text{ Å} \\
b &= 10.1969 (1) \text{ Å} \\
c &= 7.28108 (9) \text{ Å} \\
D_x &= 4.510 (1) \text{ Mg m}^{-3} \\
\lambda &= 0.998043 \text{ Å} \\
T &= 298 \text{ K} \\
\text{Specimen shape: cylinder} & \\
40 \times 0.7 \times 0.7 \text{ mm}
\end{align*}
\]
supplementary materials

$\alpha = 90^\circ$

Specimen prepared at 100 kPa

$\beta = 90^\circ$

Specimen prepared at 1258 K

$\gamma = 120^\circ$

Particle morphology: powder, white

$V = 655.63 (2) \text{ Å}^3$

Data collection

In-house design
diffractometer

Scan method: step

Monochromator: Si(111) channel-cut crystal

$T = 298 \text{ K}$

Specimen mounting: capillary

$2\theta_{\min} = 2, 2\theta_{\max} = 60^\circ$

Specimen mounted in transmission mode

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

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/\sigma)_{\text{max}} = 0.001$

Wavelength of incident radiation: 0.998043 Å

Prefered 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$^2$)

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{iso}$/$U_{eq}$</th>
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<td>0.015 (4)</td>
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<td>Cl1</td>
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<td>0.0000</td>
<td>0.0000</td>
<td>0.031 (5)</td>
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Geometric parameters (Å, °)

$\text{Sr1}—\text{O1}^i$ 2.49 (2) $\text{Sr2}—\text{O3}^vi$ 2.44 (1)

$\text{Sr1}—\text{O1}^ii$ 2.49 (2) $\text{Sr2}—\text{O3}^vii$ 2.94 (1)

$\text{Sr1}—\text{O1}$ 2.49 (2) $\text{Sr2}—\text{O3}^{viii}$ 2.94 (1)

$\text{Sr1}—\text{O2}^iii$ 2.59 (2) $\text{Sr2}—\text{O1}^ii$ 3.02 (2)

$\text{Sr1}—\text{O2}^iv$ 2.59 (2) $\text{Sr2}—\text{Cl1}^{viii}$ 3.156 (3)
supplementary materials

<table>
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<tr>
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<td>O3—As1—O1</td>
<td>105.8 (7)</td>
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<tr>
<td>O3&lt;sup&gt;x&lt;/sup&gt;—As1—O1</td>
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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

Sr$_5$(AsO$_4$)$_3$Cl 9.1 data
Lambda 0.9980 A, L-S cycle 228
Obsd. and Diff. Profiles
supplementary materials

Fig. 2