

Sr, Ba and Cd arsenates with the apatite-type structure

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X-ray diffraction analysis of single crystals of three new arsenates adopting apatite-type structures yielded formula $\text{Sr}_5(\text{AsO}_4)_3\text{F}$ for strontium arsenate fluoride, (I), $(\text{Sr}_{1.66}\text{Ba}_{0.34})\text{-(Ba}_{2.61}\text{Sr}_{0.39})(\text{AsO}_4)_3\text{Cl}$ for strontium barium arsenate chloride, (II), and $\text{Cd}_5(\text{AsO}_4)_3\text{Cl}_{0.58}(\text{OH})_{0.42}$ for cadmium arsenate hydroxide chloride, (III). All three structures are built up of isolated slightly distorted AsO_4 tetrahedra that are bridged by Sr^{2+} in (I), by $\text{Sr}^{2+}/\text{Ba}^{2+}$ in (II) and by Cd^{2+} in (III). Compounds (I) and (II) represent typical fluorapatites and chlorapatites, respectively, with F^- at the $2a$ $(0, 0, \frac{1}{4})$ site and Cl^- at the $2b$ $(0, 0, 0)$ site of $P6_3/m$. In contrast, in (III), due to the requirement that the smaller Cd^{2+} cation is positioned closer to the channel Cl^- anion (partially substituted by OH^-), the anion occupies the unusual $2a$ $(0, 0, \frac{1}{4})$ site. Therefore, Cl^- is similar to F^- in (I), coordinated by three A2 cations, unlike the octahedrally coordinated Cl^- in (II) and other ordinary chlorapatites. Furthermore, in (III), using FT-IR studies, we have inferred the existence of H^+ outside the channel in oxyhydroxyapatites and provided possible atomic coordinates for a H atom in HAsO_4^{2-} , leading to a proposed formulation of the compound as $\text{Cd}_5(\text{AsO}_4)_3\text{-}_x(\text{HAsO}_4)_x\text{-Cl}_{0.58}(\text{OH})_{0.42-x-(y/2)}\text{O}_{x+(y/2)}\square_{y/2}$.

Comment

Minerals of composition $\text{Ca}_5(\text{PO}_4)_3\text{X}$, where $\text{X} = \text{OH}^-$, F^- , Cl^- , CO_3^{2-} , etc., have been investigated for a long time and classified as apatites. The same name has also been used to represent the structural type of compounds with the general formula $(\text{A1})_2(\text{A2})_3(\text{ZO}_4)_3\text{X}$, where A1 and A2 are distinct crystallographic sites that usually accommodate large divalent (Ca^{2+} , Sr^{2+} , Pb^{2+} , Ba^{2+} , Cd^{2+} , etc.), monovalent (Li^+ , Na^+ , K^+ , etc.) or trivalent (Y^{3+} , La^{3+} , Ce^{3+} , Nd^{3+} , Sm^{3+} , etc.) cations. The Z sites are filled with small highly charged cations (P^{5+} , As^{5+} , V^{5+} , Si^{4+} , S^{6+} , etc.) and the X anion site is occupied by halides,

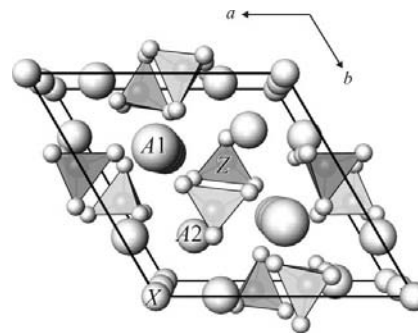


Figure 1
The crystal structure of apatite-type compounds.

OH^- or O^{2-} , CO_3^{2-} , SO_4^{2-} , water molecules, vacancies, etc. The structure type allows complex chemical substitutions, with the charge balance being achieved by coupled cation substitutions or by the mixing of mono- and divalent X anions and/or X-site vacancies (Mercier *et al.*, 2005). Natural and synthetic apatite-type materials have applications in geochronology, catalysis, environmental remediation, bone replacement, dentistry and soil treatment. Members of the apatite family are emerging as important immobilization matrices because they can incorporate a range of toxic elements (Baikie *et al.*, 2008). The crystal structures of apatites and related compounds have recently been reviewed (White & ZhiLi, 2003).

The large majority of the compounds that belong to the apatite family are hexagonal. The most common space group is $P6_3/m$ with $Z = 2$ and unit-cell contents $(\text{A1})_4(\text{A2})_6(\text{ZO}_4)_6\text{X}_2$. A characteristic feature of the apatite structure type is the presence of channels along the c_3 axes, where the X anions are situated. The A1 cations have site symmetry 3 and are located at the $4f$ Wyckoff position. They are connected to six ZO_4 tetrahedra, three of which chelate to A1 while the other three are corner-connected to the cation (Fig. 1). Therefore, the coordination number of A1 is nine with six shorter and three longer bonds to O atoms. The six shorter bonds (three to O1 and three to O2) define a distorted trigonal prismatic geometry, *i.e.* a polyhedron that is intermediate between a trigonal prism and an octahedron. Capping the prism faces, three O3 atoms at longer distances are located near the equatorial plane of the tricapped trigonal prism. The $(\text{A1})_6$ polyhedra share basal trigonal faces to form chains parallel to the c axis. According to a recent contribution (Mercier *et al.*, 2005), the lattice parameter a is determined by the $(\text{A1})_6\text{-ZO}_4$ polyhedral arrangement. Neighbouring A1- and A2-centred polyhedra are linked through O atoms of the ZO_4 tetrahedra. The A2 cations situated in the $6h$ Wyckoff position are usually coordinated by six O atoms (O1, O2 and four O3) and one or two X anions. The coordination of A2 depends on the identity and atomic position of X. Generally, the $2a$ site $(0, 0, \frac{1}{4})$ is occupied by F^- in fluorapatites, while the $2b$ site $(0, 0, 0)$ is occupied by Cl^- in chlorapatites. The F^- anion is coordinated by three A2 atoms in a trigonal planar geometry, while the Cl^- anion is coordinated by six A2 atoms in a regular octahedral environment. Therefore, when X is a

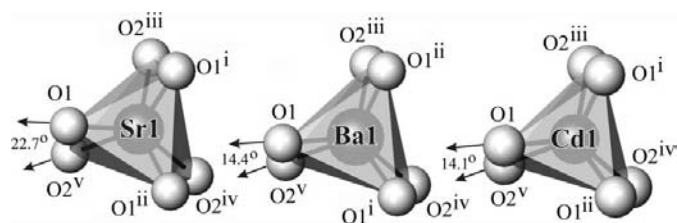


Figure 2

Metaprisms twist angles in the A1-centred polyhedra of (I) (left), (II) (centre) and (III) (right). [Symmetry codes: (i) $-x + y, -x + 1, z$; (ii) $-y + 1, x - y + 1, z$; (iii) $x - y, x, -z$; (iv) $y, -x + y + 1, -z$; (v) $-x + 1, -y + 1, -z$.]

smaller anion such as F^- or OH^- , the coordination number of A2 is seven, and when X is a larger anion, such as Cl^- , Br^- or I^- , the coordination number of A2 is eight. A2 bridges five ZO_4 tetrahedra, one of which also has chelating character. According to Mercier *et al.* (2005), the $-A2-O3-Z-O3-A2-$ chains, located in the channels extending along the hexagonal axis, control the magnitude of the c lattice parameter.

As part of a comprehensive study of the hydrothermal synthesis, crystallography and properties of arsenate and vanadate compounds in the system $M1-M2-Z-O-H$ ($M1 = Sr^{2+}, Cd^{2+}, Ba^{2+}, Bi^{3+}, Hg^{2+}$; $M2 = Mg^{2+}, Mn^{2+,3+}, Fe^{2+,3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}$; $Z = As^{5+}, V^{5+}$), this paper reports the hydrothermal synthesis of three new compounds belonging to the apatite structure type, *viz.* $Sr_5(AsO_4)_3F$, (I), $(Sr_{1.66}Ba_{0.34})(Ba_{2.61}Sr_{0.39})(AsO_4)_3Cl$, (II), and $Cd_5(AsO_4)_3Cl_{0.58}(OH)_{0.42}$, (III), which have been characterized chemically, structurally and, for (I) and (III), by FT-IR spectroscopy.

In all three compounds, the A1 atom is coordinated by nine O atoms. The coordination polyhedra have the form of a slightly distorted tricapped trigonal prism. Bond distances in (I) and (III) are similar to those found in $Sr_5(PO_4)_3Br$ (Nötzold & Wulff, 1998), as well as in $Cd_5(AsO_4)_3Cl_{1-2x}O_x(OH)_y$ (Johnson *et al.*, 2004) and $Cd_5(PO_4)_3Cl$ (Sudarsanan *et al.*, 1973). In (II), the A1 crystallographic site is jointly occupied by Sr^{2+} and Ba^{2+} . Due to the presence of 17% Ba^{2+} , which is a larger cation than Sr^{2+} , the A1–O distances are longer than those found in (I).

According to White & ZhiLi (2003), systematic crystallographic changes in apatite-type solid solution series may be described practically as deviations from regular anion nets, with particular focus on the O1–A1–O2 twist angle φ projected on (001) of the $(A1)O_6$ prism. Therefore, the coordination polyhedron around A1 can also be described as a disordered trigonal prism with two bases formed by $O1_3$ and $O2_3$ triangles twisted with respect to one other by an angle of φ . For apatites that contain the same A cation, it is shown (White & ZhiLi, 2003) that φ decreases linearly as a function of increasing average ionic radius of the formula, and for the idealized fluorapatite $[Ca_5(PO_4)_3F]$ and chlorapatite $[Ca_5(PO_4)_3Cl]$ structures it should be 23.3 and 19.1°, respectively. In the title structures, these angles are 22.7, 14.4 and 14.1° for (I), (II) and (III), respectively (Fig. 2). The substitution of



Figure 3

Coordination polyhedra around the A2 site in (I) (left), (II) (centre) and (III) (right). [Symmetry codes: (i) $-x + y, -x + 1, z$; (ii) $-y + 1, x - y + 1, z$; (iii) $x - y, x, -z$; (iv) $y, -x + y + 1, -z$; (v) $x, y + 1, z$; (vi) $y, -x + y + 1, z + \frac{1}{2}$; (vii) $x, y + 1, -z + \frac{1}{2}$; (viii) $-x, -y + 1, z + \frac{1}{2}$; (ia) $-x + y, -x, z$; (iaa) $-y + 1, x - y, z$; (iva) $y, -x + y, -z$; (via) $y, -x + y, z + \frac{1}{2}$; (viiia) $x, y, -z + \frac{1}{2}$.]

larger cations for smaller (As for P, as well as Ba and Sr for Ca) increases the unit-cell volume and decreases the φ value. In addition, a further decrease of φ is due to mixed ion occupancies in positions A1 and A2 in (II), and X in (III).

The $(A2)O_6X_{1,2}$ polyhedra are basically irregular (Fig. 3). The A2 site is coordinated by O^{2-} and X^- anions and its coordination number depends on the individual structures. The Sr2 cations in (I) are coordinated by six O atoms (O1, O2 and four O3) and one F1. The A2 position in (II) is shared by 87% Ba^{2+} and 13% Sr^{2+} and the mean A2–O distance is 2.855 Å. The Cd2 atom located on the A2 site in (III) is coordinated by five O atoms and one Cl/O, *viz.* $(Cd2)O2(O3)_4(Cl1,O4)$, with one pair of O3 atoms closer to Cd2 [2.208 (3) Å] than the other pair [2.426 (3) Å]. The sixth O atom is at a long distance [Cd2–O1 = 3.372 (5) Å] and contributes to the bond valence by approximately 2%.

In the channels extending along the c axis, F1 anions occupy the $2a$ $(0, 0, \frac{1}{4})$ position in (I) and are coordinated by three equidistant Sr2 atoms. The Sr2–F1 bond lengths are a little shorter than the value of 2.51 Å calculated from ionic radii (Shannon, 1976), but similar to the value of 2.441 (5) Å found in $Sr_5(CrO_4)_3F$ (Baikie *et al.*, 2007). The F1 atom in (I) shows an elongated ellipsoid [principal mean-square atomic displacements $U = 0.016$ (2), 0.016 (2) and 0.083 (5) Å²], with the axis of elongation oriented normal to the $F1(Sr2)_3$ plane, which suggests a statistical positional disorder and a potential splitting of this position.

In (II), the Cl1 anion, located at the $2b$ $(0, 0, 0)$ site, is coordinated by six A2 atoms. The $Cl1(A2)_6$ coordination is a regular octahedron with a Cl1–A2 distance of 3.2298 (5) Å, which agrees well with the calculated Cl–Ba distance of 3.23 Å, as well as with the Cl–Ba distance of 3.230 (1) Å found in $Ba_5(PO_4)_3Cl$ (Hata *et al.*, 1979).

In (III), atoms Cl1 and O4 share the same $2a$ $(0, 0, \frac{1}{4})$ position, with refined occupancies of 0.58 (3) and 0.42 (3), respectively, which results in the formula $Cd_5(AsO_4)_3Cl_{0.58}(OH)_{0.42}$ (Fig. 4). Bond-valence analysis of the X site in (III) showed an almost ideal value (1.02 v.u.), in contrast with the value of 1.29 v.u. found for the X position fully occupied by Cl (Johnson *et al.*, 2004). The incorporation of the smaller OH^- group at this anion site is reflected by the short X–X

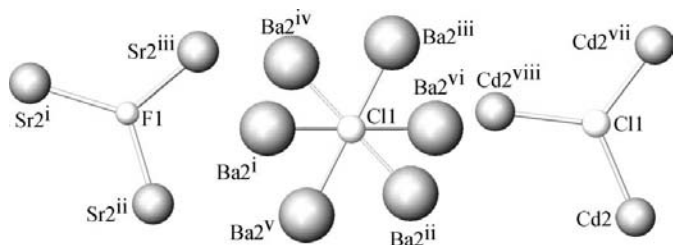


Figure 4
 Coordination environment of the *X* site in (I) (left), (II) (centre) and (III) (right). [Symmetry codes: (i) $-x + y - 1, -x, z$; (ii) $-y + 1, x - y + 1, z$; (iii) $x, y - 1, z$; (iv) $y - 1, -x + y - 1, -z$; (v) $-x, -y + 1, -z$; (vi) $x - y + 1, x, -z$; (vii) $-x + y + 1, -x, z$; (viii) $-y + 1, x - y, z$.]

distance (observed 3.26 Å *versus* calculated 3.62 Å for the sum of $\text{Cl}^- + \text{Cl}^-$ ionic radii, and 3.21 Å for the sum of $\text{Cl}^- + \text{O}^{2-}$ ionic radii). Similar to the H-atom positions in $\text{Ca}_{10}(\text{PO}_4)_{6-x}(\text{HPO}_4)_x(\text{OH})_y\text{O}_z$ (Arcos *et al.*, 2004), we located and included atom H4 in the refinement as a riding atom at the same occupancy as the attached O4 atom and with a restrained distance to O4. If the amount of hydrogen bonding in the channel were 100%, the results of the structure refinement would show that approximately $\frac{2}{3}$ Cl1 receives one hydrogen bond. If atom O4 in the structure of (III) was interpreted as an oxide, not as a hydroxide, then the charge balance would lead to the creation of vacancies in the $2a$ ($0, 0, \frac{1}{4}$) position and/or additional OH^- groups somewhere else in the structure.

The somewhat longer As1–O2 bond distance of 1.706 (4) Å, together with a broad band of low intensity at approximately 3491 cm^{-1} in the IR spectrum, which correlates with an $\text{O}_\text{h} - \text{H} \cdots \text{O}$ distance of 2.95 Å, also suggest that at least a small portion of the $(\text{As}1)\text{O}_4$ tetrahedra may be protonated. The O–As1–O angles are consistent with this interpretation. Compared with the ideal tetrahedral angle of 109.47° , two O–As1–O angles are smaller [103.3 (2) and 105.73 (15) $^\circ$] and two are larger [111.0 (2) and 115.09 (14) $^\circ$]. Similar crystal chemical behaviour was found for protonated phosphates (Baur, 1974). This theory is also in accordance with the bond valences (Brese & O’Keeffe, 1991).

Considering only the contributions of Cd and As, atom O2 is under-saturated (1.74 v.u.), as is characteristic of donor O atoms of hydroxyl groups involved in hydrogen bonds with $\text{O} \cdots \text{O}$ distances > 2.90 Å. Therefore, the most probable formula for (III) is $\text{Cd}_5(\text{AsO}_4)_{3-x}(\text{HAsO}_4)_x\text{Cl}_{0.58}(\text{OH})_{0.42-x}\text{O}_x$. Because the possibility of additional minor vacancies at the $2a$ site ($2\text{OH}^- \rightarrow \text{O}^{2-} + \square$) cannot be excluded, the formula of (III) is finally proposed to be $\text{Cd}_5(\text{AsO}_4)_{3-x}(\text{HAsO}_4)_x\text{Cl}_{0.58}(\text{OH})_{0.42-x-(y/2)}\text{O}_{x+(y/2)}\square_{y/2}$.

A feature was observed in the difference map at approximately $x = 0.70, y = 0.50$ and $z = 0.25$ that could be interpreted as a H atom belonging to the partially protonated $(\text{As}1\text{O}_4)^{3-}$ group [$\text{O}2 - \text{O}2^i = 2.970$ (2) Å; symmetry code: (i) $-y + 1, x - y, z$]. However, because of the low scattering power of the H atoms it was impossible to determine partial occupancies from the X-ray data. Therefore, we did not attempt to include this H atom in the refinement.

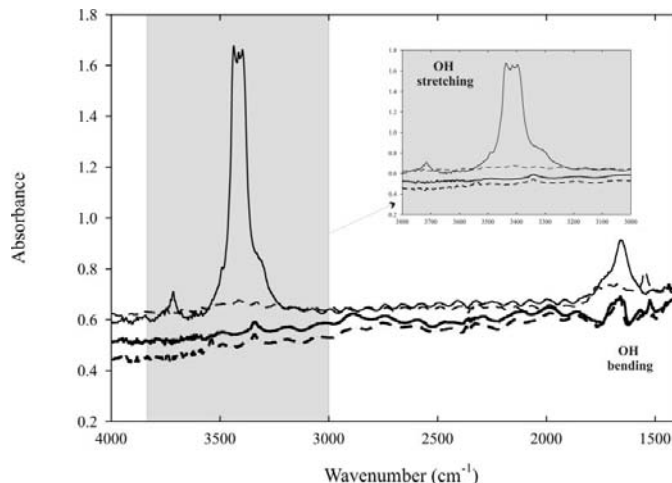


Figure 5
 Polarized single-crystal FT-IR spectra of (I) (bold) and (III).

Experimental

Single crystals of $\text{Sr}_5(\text{AsO}_4)_3\text{F}$, (I), $(\text{Sr}_{1.66}\text{Ba}_{0.34})(\text{Ba}_{2.61}\text{Sr}_{0.39})(\text{AsO}_4)_3\text{Cl}$, (II), and $\text{Cd}_5(\text{AsO}_4)_3\text{Cl}_{0.58}(\text{OH})_{0.42}$, (III), were obtained as reaction products from the following mixtures (approximate 1:1:1 molar ratio in each case): $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (Merck, >97%), $\text{Co}(\text{OH})_2$ (Alfa Products) and As_2O_5 (Alfa Products, >99.9%) for (I); $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (Mallinckrodt, >97%), $\text{Co}(\text{OH})_2$ and As_2O_5 for (II); and $\text{Cd}(\text{OH})_2$ (Alfa Products), Cu powder, and $3\text{As}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ (Merck, 99%) for (III). The mixtures were transferred into Teflon vessels and filled to approximately 70% of their inner volume with distilled water. Finally, they were enclosed in stainless steel autoclaves. The subsequently determined presence of F in (I), Sr and Cl in (II) and Cl in (III) is caused by either impurities from the chemicals themselves or from residual impurities in the Teflon vessels, or by extraction of F^- from the Teflon vessels by the hydrothermal fluid.

The mixture for (I) was heated under autogenous pressure from 293 to 493 K over a period of 4 h, held at this temperature for 48 h, cooled to 423 K over a period of 10 h, kept at this temperature for 10 h, cooled to 373 K over a period of 10 h, kept at this temperature for 10 h, and finally cooled to room temperature over a period of 10 h. Compound (I) crystallizes as colourless prismatic crystals up to 0.11 mm in length, together with a volumetrically similar quantity of pink prismatic crystals of $\text{SrCo}(\text{AsO}_4)(\text{OH})$ (Brese & O’Keeffe, 1991). The mixture for (II) was heated under autogenous pressure from room temperature to 493 K over a period of 6 h, held at that temperature for 6 d and cooled slowly to room temperature overnight. Compound (II) crystallizes as colourless prismatic crystals up to 0.12 mm in length, accompanied by a greater quantity of hexagonal tabular dark-pink crystals of $\text{BaCo}_2(\text{AsO}_4)_2$ (Mihajlović, 2005). The mixture for (III) was heated under autogenous pressure from room temperature to 493 K over a period of 6 h, held at that temperature for 4 d and spontaneously cooled to room temperature. Compound (III) crystallizes as colourless transparent prismatic crystals up to 0.20 mm in length, together with pink prismatic crystals of $\text{CdCo}(\text{AsO}_4)(\text{OH})$ (Brese & O’Keeffe, 1991) and $\text{Co}_{1-x}(\text{OH})_3(\text{AsO}_4\text{H}_{2x/3})(\text{HAsO}_4)$ (Hughes *et al.*, 2003). All reaction products were filtered, washed thoroughly with distilled water and dried in air at room temperature.

Qualitative chemical analyses performed using a Jeol JSM-6400LV scanning electron microscope (SEM) connected to a LINK energy-dispersive X-ray analysis (EDX) unit confirmed the presence of Sr

and As in (I), Ba, Sr, As and Cl in (II), and Cd, As and Cl in (III). The sensitivity of the instrument did not allow F to be observed in (I).

In order to investigate the water content of compounds (I) and (III), polarized single-crystal FT-IR spectra in the range 4000–400 cm^{-1} were recorded on a Bruker Tensor 27 spectrophotometer coupled with a Hyperion microscope. The presence of hydrogen bonding can be detected by IR spectroscopy in the domains of the OH^- stretching modes. As expected for an OH-free apatite, OH^- stretching bands were not observed for (I), while for (III) OH^- stretching vibrations at approximately 3715, 3437, 3414, 3405 and 3396 cm^{-1} were observed when the polarization beam was parallel to the elongation of the crystal (Fig. 5). In the spectrum, a high-wavenumber band of low intensity is observed at 3491 cm^{-1} , which may be attributed to the stretching vibration of an $(\text{HAsO}_4)^{2-}$ unit. According to $d-\nu$ correlations for hydrogen bonds (Libowitzky, 1999), the OH^- stretching vibrations around 3490 cm^{-1} correlate with $\text{O}_h-\text{H}\cdots\text{O}$ interactions of ~ 2.95 Å. It is quite characteristic that O–H stretching bands can only be observed in one of the polarized spectra, whereas they are absent in the other polarization directions (when elongation of the crystal was perpendicular to the polarization of the beam). The orientation dependence is caused by the preferred orientation of the OH^- groups (O–H vectors) in the crystal structure. Broadening bands attributed to absorbed water were also observed at about 3330 and 1650 cm^{-1} . Due to the strong absorption and the small amount of sample, bands under 1000 cm^{-1} could not be analyzed. Crystals of (II) were not investigated by FT-IR spectroscopy because chemical analyses and structure refinements indicate that the X site is fully occupied by Cl^- .

Compound (I)

Crystal data

$\text{Sr}_5(\text{AsO}_4)_3\text{F}$	$Z = 2$
$M_r = 873.86$	Mo $K\alpha$ radiation
Hexagonal, $P6_3/m$	$\mu = 28.51 \text{ mm}^{-1}$
$a = 9.990$ (1) Å	$T = 294$ (2) K
$c = 7.395$ (1) Å	$0.09 \times 0.04 \times 0.02$ mm
$V = 639.15$ (13) Å ³	

Data collection

Nonius KappaCCD diffractometer	4782 measured reflections
Absorption correction: multi-scan (SCALEPACK; Otwinowski & Minor, 1997; Otwinowski <i>et al.</i> , 2003)	438 independent reflections
	421 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.036$
$T_{\text{min}} = 0.263$, $T_{\text{max}} = 0.567$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.017$	40 parameters
$wR(F^2) = 0.037$	$\Delta\rho_{\text{max}} = 0.59 \text{ e } \text{Å}^{-3}$
$S = 1.22$	$\Delta\rho_{\text{min}} = -0.53 \text{ e } \text{Å}^{-3}$
438 reflections	

Compound (II)

Crystal data

$(\text{Sr}_{1.66}\text{Ba}_{0.34})(\text{Ba}_{2.61}\text{Sr}_{0.39})(\text{AsO}_4)_3\text{Cl}$	$Z = 2$
$M_r = 1036.98$	Mo $K\alpha$ radiation
Hexagonal, $P6_3/m$	$\mu = 22.95 \text{ mm}^{-1}$
$a = 10.390$ (1) Å	$T = 294$ (2) K
$c = 7.575$ (2) Å	$0.09 \times 0.04 \times 0.04$ mm
$V = 708.2$ (2) Å ³	

Data collection

Nonius KappaCCD diffractometer	1672 measured reflections
Absorption correction: multi-scan (SCALEPACK; Otwinowski & Minor, 1997; Otwinowski <i>et al.</i> , 2003)	455 independent reflections
	422 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.016$
$T_{\text{min}} = 0.344$, $T_{\text{max}} = 0.401$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.020$	42 parameters
$wR(F^2) = 0.049$	$\Delta\rho_{\text{max}} = 0.82 \text{ e } \text{Å}^{-3}$
$S = 1.11$	$\Delta\rho_{\text{min}} = -0.69 \text{ e } \text{Å}^{-3}$
455 reflections	

Compound (III)

Crystal data

$\text{Cd}_5(\text{AsO}_4)_3\text{Cl}_{10.58}(\text{OH})_{0.42}$	$Z = 1$
$M_r = 2012.93$	Mo $K\alpha$ radiation
Hexagonal, $P6_3/m$	$\mu = 18.31 \text{ mm}^{-1}$
$a = 9.971$ (1) Å	$T = 294$ (2) K
$c = 6.514$ (1) Å	$0.07 \times 0.05 \times 0.05$ mm
$V = 560.86$ (12) Å ³	

Data collection

Nonius KappaCCD diffractometer	4589 measured reflections
Absorption correction: multi-scan (SCALEPACK; Otwinowski & Minor, 1997; Otwinowski <i>et al.</i> , 2003)	424 independent reflections
	420 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.025$
$T_{\text{min}} = 0.348$, $T_{\text{max}} = 0.396$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.018$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.037$	$\Delta\rho_{\text{max}} = 1.03 \text{ e } \text{Å}^{-3}$
$S = 1.30$	$\Delta\rho_{\text{min}} = -1.05 \text{ e } \text{Å}^{-3}$
424 reflections	
42 parameters	
1 restraint	

Table 1

Selected bond lengths (Å) and angles (°) for (I), (II) and (III).

	(I)	Mean (II)	Mean (III)	Mean
A1–O3 ($\times 3$)	2.957 (3)	2.993 (6)	2.960 (3)	
A1–O2 ($\times 3$)	2.616 (2)	2.647 (4)	2.375 (3)	
A1–O1 ($\times 3$)	2.543 (2)	2.705 2.611 (4)	2.750 2.296 (3)	2.544
A2–O3 ($\times 2$)	2.671 (2)	2.607 (4)	2.426 (3)	
A2–O3 ($\times 2$)	2.515 (2)	2.906 (5)	2.208 (3)	
A2–O2	2.530 (3)	2.604 (6)	2.368 (4)	
A2–O1	2.821 (3)	3.127 (6)	3.372 (5)	
A2–X	2.4328 (5)	2.594 3.2298 (5)	2.855 2.5191 (6)	2.500
As1–O3 ($\times 2$)	1.674 (2)	1.668 (4)	1.686 (3)	
As1–O2	1.677 (3)	1.681 (5)	1.706 (4)	
As1–O1	1.680 (3)	1.676 1.688 (5)	1.676 1.656 (4)	1.683
X–X	3.698	3.788	3.257	
O3–As1–O3	106.40 (17)	108.0 (3)	103.3 (2)	
O3–As1–O1 ($\times 2$)	111.44 (10)	112.43 (19)	115.09 (14)	
O3–As1–O2 ($\times 2$)	107.56 (11)	106.1 (2)	105.73 (15)	
O1–As1–O2	112.15 (16)	109.4 111.4 (3)	109.4 111.0 (2)	109.3

The refinements were started from the reported parameters of fluorapatite and chlorapatite (White & ZhiLi, 2003). In (II), a substitutional disorder was apparent and the occupancies of Ba^{2+} and Sr^{2+} in both the A1 and A2 positions were refined, keeping the occupancy sum of $\text{Ba1}+\text{Sr1}$ fixed at four and $\text{Ba2}+\text{Sr2}$ fixed at six atoms per unit cell to satisfy the charge balance. The atomic coordinates and displacement parameters of Ba1 and Sr1 and of Ba2 and

Sr2 were kept equal. Occupancy factors of 0.17 (1) and 0.83 (1) for Ba1 and Sr1, respectively, and 0.87 (1) and 0.13 (1) for Ba2 and Sr2 were obtained. A similar procedure was applied for Cl1 and O4, which both occupy the X site in (III). In this structure, Cl1 [0.58 (3)] and O4 [0.42 (3)] were found at the same (0, 0, $\frac{1}{4}$) position and their sum was fixed at two atoms per unit cell. Occupancy refinements of the F1 (X) site in (I) gave a value of 1.00, which, along with the FT-IR spectrum (see above), confirms that no (or only negligible) OH is located on this site.

For all compounds, data collection: *COLLECT* (Nonius, 2002); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *WinGX* (Farrugia, 1999) and *SHELXL97* (Sheldrick, 2008); molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *pubCIF* (Westrip, 2008).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3149). Services for accessing these data are described at the back of the journal.

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