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CsAlZr$_2$(PO$_4$)$_4$: an anhydrous aluminium zirconium phosphate with a novel three-dimensional framework

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Caesium aluminium dizirconium tetrakis[phosphate(V)], CsAlZr$_2$(PO$_4$)$_4$, has been synthesized by high-temperature reaction and studied by single-crystal X-ray diffraction at room temperature. This represents the first detailed structural analysis of an anhydrous phosphate containing both zirconium and aluminium. The structure features a complicated three-dimensional framework of [AlZr$_2$(PO$_4$)$_4$] constructed by PO$_4$, AlO$_4$ and ZrO$_6$ polyhedra interconnected *via* corner-sharing O atoms, and one-dimensional Cs chains which are located in the infinite tunnels within the [AlZr$_2$(PO$_4$)$_4$] framework, which run along the *c* axis. The Cs, Al, one P and two O atoms lie on a mirror plane, while a second P atom lies on a twofold axis.

Comment

Anhydrous inorganic metal phosphates prepared by high-temperature solid-state reactions have been the subject of intensive research activities and their number has grown steadily (Kanatzidis *et al.*, 2007; Ettis *et al.*, 2003; Zaripov *et al.*, 2009; Zatovsky *et al.*, 2007; Xiong *et al.*, 2007; Ranmohotti *et al.*, 2006; Parreu *et al.*, 2006). The crystal chemistry of these compounds with partial structures mainly built from PO$_4$ tetrahedral building units reveals a large structural variety, which is usually accompanied by intriguing magnetism, electric, optical and thermal expansion properties. Furthermore, chemical and thermal stability ensures their wide application in many fields. Introduction of M^{IV} (M = Ti, Zr, Ge, Sn) cations into the phosphates can result in many different three-dimensional frameworks with the basic unit of MO$_6$ octahedra and PO$_4$ tetrahedra, such as KTiPO$_5$ (Tordjman *et al.*, 1974) and NaZr$_2$(PO$_4$)$_3$ (Hagman *et al.*, 1968). For Zr^{IV} cations, the reported phosphates include KZr$_2$(PO$_4$)$_3$ (Sljukic *et al.*, 1969), K$_4$CeZr(PO$_4$)$_4$ (Ogorodnyk *et al.*, 2006), Na$_3A$Zr(PO$_4$)$_3$ (A = Mg, Ni; Chakir *et al.*, 2006), A_2Mg$_{0.5}$Zr$_{1.5}$(PO$_4$)$_3$ (A = K, Rb, Cs; Orlova *et al.*, 2005) and NaNbZr(PO$_4$)$_3$ (Bennouna *et al.*,

1995), *etc.* We expected that the introduction of AlO$_4$ groups, which may serve as bridges between ZrO$_6$ and PO$_4$ building units, would result in new zirconium phosphate compounds with novel architectures. Our research efforts in this regard have led to the novel caesium aluminium zirconium phosphate compound CsAlZr$_2$(PO$_4$)$_4$. To the best of our knowledge, this represents the first compound in the quinary Cs/Al/Zr/P/O system.

CsAlZr$_2$(PO$_4$)$_4$ crystallizes in the orthorhombic space group *Pbcm*, with 15 crystallographically independent atoms, *viz.* one Cs, one Al, one Zr, three P and nine O atoms. Fig. 1 illustrates a selected unit of the compound, which highlights that the Zr atom is six-coordinated by O atoms in an octahedral geometry. The Zr—O bond distances are in the range 2.038 (3)–2.095 (3) Å, with a mean value of 2.067 (3) Å, which is in good agreement with those found in other zirconium(IV) compounds, such as BaZr(PO$_4$)$_2$ (Bregiroux *et al.*, 2009), Zr$_2$(MoO$_4$)(PO$_4$)$_2$ (Cetinkol *et al.*, 2009) and Rb$_2$Zr(IO$_3$)$_6$ (Shehee *et al.*, 2005). The P and Al atoms are all tetrahedrally coordinated by O atoms. The P—O distances fall in the range 1.510 (3)–1.540 (3) Å, and the O—P—O angles range from 105.7 (2) to 112.40 (17)°, which is comparable to those reported in other metal phosphates (Ettis *et al.*, 2003; Zhao *et al.*, 2010). The Al—O bond distances fall in the range 1.720 (4)–1.729 (4) Å, and the O—Al—O angles range from 102.9 (2) to 115.13 (13)°, which is similar to those reported in other aluminium(III) compounds, such as Ca$_{12}$Al$_{14}$O$_{32}$Cl$_2$ (Iwata *et al.*, 2008) and Sr(Al$_2$Si$_2$O$_8$) (Nedic *et al.*, 2008).

The structure of CsAlZr$_2$(PO$_4$)$_4$ features a complicated three-dimensional framework of [AlZr$_2$(PO$_4$)$_4$] constructed by interconnected PO$_4$, AlO$_4$ and ZrO$_6$ polyhedra. Fig. 2 shows the connectivity of the polyhedra. All PO$_4$ tetrahedra are isolated from one another, and they are linked to adjacent
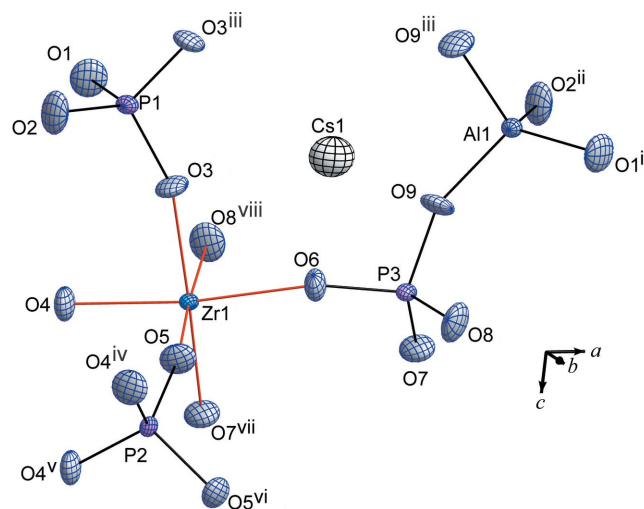

Figure 1
The asymmetric unit of CsAlZr$_2$(PO$_4$)$_4$, expanded to show the coordination environments of the Zr1, Al1, P1, P2 and P3 atoms. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $1 - x, \frac{1}{2} + y, z$; (ii) $1 + x, y, z$; (iii) $x, y, \frac{3}{2} - z$; (iv) $-x, \frac{1}{2} + y, z$; (v) $-x, 1 - y, 2 - z$; (vi) $x, \frac{3}{2} - y, 2 - z$; (vii) $1 - x, 1 - y, 2 - z$; (viii) $1 - x, -\frac{1}{2} + y, z$.]

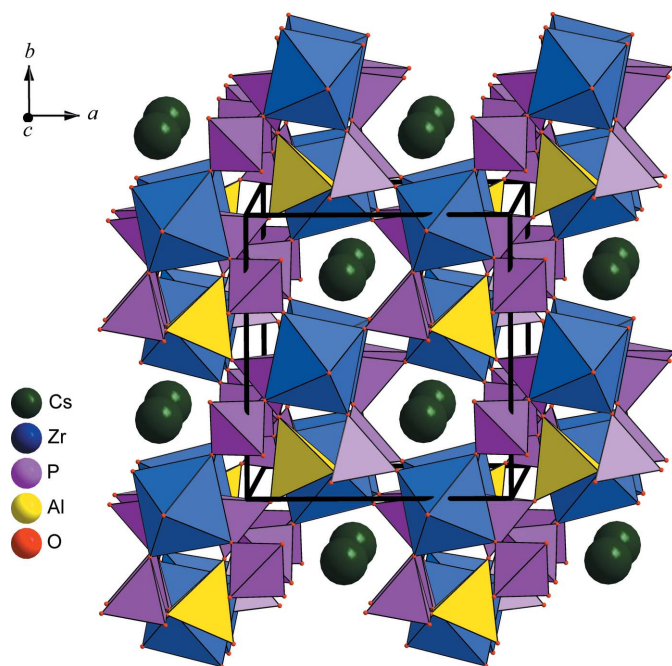**Figure 2**
A view of the three-dimensional crystal structure of $CsAlZr_2(PO_4)_4$. Cs1—O bonds have been omitted for clarity.
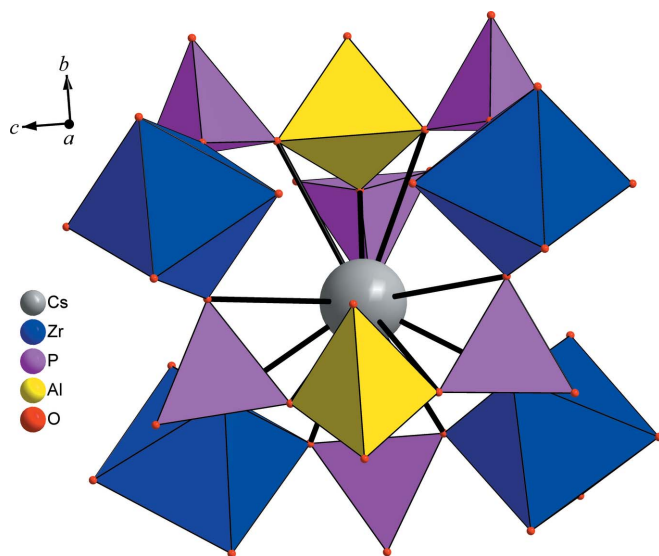

Figure 3
A view of the coordination of the Cs1 atom.

polyhedra only by corner-sharing O atoms. The P1O$_4$ tetrahedron is coordinated by two AlO$_4$ and two Zr1O$_6$ polyhedra, the P2O$_4$ tetrahedron is coordinated by four Zr1O$_6$ octahedra, and P3O$_4$ is coordinated by one Al1O$_4$ tetrahedron and three Zr1O$_6$ octahedra. The Zr1O$_6$ polyhedron is coordinated by six PO$_4$ tetrahedra, that is, three P3O$_4$, two P2O$_4$ and one P1O$_4$ polyhedron. On the other hand, AlO$_4$ tetrahedra are also isolated from each other: four corners are shared with two P1O$_4$ and two P3O$_4$ polyhedra. It is notable that all nine symmetry-independent O atoms participate in μ_2-bridging. All of the above-mentioned groups, AlO$_4$, ZrO$_6$ and

PO$_4$ are interconnected *via* corner-sharing O atoms to form the three-dimensional framework of $[AlZr_2(PO_4)_4]$.

Furthermore, the $[AlZr_2(PO_4)_4]$ framework contains infinite tunnels along the *c* axis in which the Cs atoms are located through Coulombic action of Cs$^+$ cations and O^{2-} anions to form the final structure of $CsAlZr_2(PO_4)_4$. It is interesting to note that the Cs atoms are in a linear array with a Cs$\cdots$Cs distance of 8.9897 (6) Å. Considering the coordination of Cs atoms, they have an 11-fold coordination of O atoms, which come from two AlO$_4$, four ZrO$_6$ and six PO$_4$ groups, as shown in Fig. 3. The Cs—O bond distances range from 3.131 (4) to 3.658 (3) Å. Compounds containing 11-coordinated Cs atoms have been reported in the literature, for example, CsPr(PO$_3$)$_4$ (Horchani-Naifer & Férid, 2007), CsGd(PO$_3$)$_4$ (Naïli & Mhiri, 2005) and Cs$_2$GeP$_4$O$_{13}$ (Zhao *et al.*, 2009).

Finally, the structure can be checked by bond-valence-sum (BVS) analysis (Brese & O'Keeffe, 1991). The calculated total BVS for Cs1, Al1, Zr1, P1, P2 and P3 are 1.005, 3.260, 4.236, 5.038, 4.886 and 5.001, respectively, which show the oxidation states of Cs, Al, Zr and P to be +1, +3, +4 and +5, respectively.

Experimental

Single crystals of $CsAlZr_2(PO_4)_4$ have been prepared by high-temperature reaction in air. A powder mixture of Cs$_2$CO$_3$ (0.8854 g), Al$_2$O$_3$ (0.1662 g), ZrO$_2$ (0.4018 g) and NH$_4$H$_2$PO$_4$ (3.000 g) in a Cs:Al:Zr:P molar ratio of 1.66:1:1:8 was first ground in an agate mortar and then transferred to a platinum crucible. The sample was gradually heated in air at 1173 K for 20 h. At this stage, the reagents were partially melted. After that, the intermediate product was cooled slowly to 773 K at a rate of 5 K h^{-1}, kept at this temperature for 10 h and then quenched to room temperature. After boiling in NH$_3$ (5%) solution, a transparent prismatic-shaped white crystal with dimensions of 0.16 × 0.10 × 0.10 mm was selected carefully from the mixture for X-ray diffraction analysis.

Crystal data

$CsAlZr_2(PO_4)_4$	$V = 1477.9$ (6) Å^3
$M_r = 722.21$	$Z = 4$
Orthorhombic, $Pbcm$	Mo $K\alpha$ radiation
$a = 8.742$ (2) Å	$\mu = 4.41$ mm^{-1}
$b = 9.403$ (3) Å	$T = 293$ K
$c = 17.979$ (3) Å	0.16 × 0.10 × 0.10 mm

Data collection

Rigaku Mercury70 CCD diffractometer	10513 measured reflections
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	1751 independent reflections
	1696 reflections with $I > 2\sigma(I)$
$T_{min} = 0.539$, $T_{max} = 0.667$	$R_{int} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$	117 parameters
$wR(F^2) = 0.068$	$\Delta\rho_{max} = 0.49$ e Å^{-3}
$S = 1.15$	$\Delta\rho_{min} = -1.79$ e Å^{-3}
1751 reflections	

The orthorhombic unit-cell parameters determined by the diffractometer were $a = 8.7417$ (5) Å, $b = 9.4031$ (8) Å and $c = 17.9793$ (13) Å. Given that the standard uncertainties (s.u. values) of unit-cell parameters calculated by the cell determination software on area-detector diffractometers are usually significantly smaller than

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the reproducibility of the parameters (Herbstein, 2000), the unit-cell s.u. values used in the final refinement and reported here have been set to values estimated to reflect more realistically the precision of the unit-cell parameters. The highest peak in the difference electron-density map is 0.06 Å from the Zr1 site and the deepest hole is 0.56 Å from the Cs1 site.

Data collection: *CrystalClear* (Rigaku, 2004); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXL97*; software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

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