

A disordered cerium(IV) phosphate with a tunnel structure, $K_4CeZr(PO_4)_4$

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Tetrapotassium cerium(IV) zirconium tetrakis(monophosphate) crystallizes in the tetragonal system (space group $I4_1/amd$). A complex disorder in $K_4CeZr(PO_4)_4$ involves the mixing of Ce and Zr atoms on a single site with $4m2$ symmetry and the splitting of P- and O-atom positions, equivalent to a rotation of the phosphate groups, to yield eight- and sixfold coordination environments around Ce and Zr, respectively. The K atoms are located in tunnels running parallel to the a and b axes.

Comment

Cerium is the only lanthanide that forms compounds in the tetravalent as well as the trivalent oxidation state. Its chemical behaviour as a tetravalent metal is similar to those of Zr, Hf, Th, U, Np and Pu. Such properties can be explained by the similar ionic radii and electron configurations of these elements (the presence of the f electrons). At the same time, there are only a few phosphates containing Ce^{IV} that have been synthesized at high temperature. At high temperatures, many Ce phosphates decompose to yield $CePO_4$ (monazite) as a main product, owing to its chemical stability (Leonardos, 1974) and its elevated melting temperature in excess of 2223 K (Ueda & Korekawa, 1955). Another stable compound containing cerium is CeP_2O_7 (Völlenkle *et al.*, 1963), which is easily prepared by the high-temperature recrystallization of the precipitate obtained by the mixing of Ce^{IV} sulfate and sodium pyrophosphate aqueous solutions. The Ce^{IV} phosphate $Ce^{IV}(PO_4)(HPO_4)_{0.5}(H_2O)_{0.5}$ can also be synthesized from CeO_2 , H_3PO_4 and H_2O (Nazaraly *et al.*, 2005). Finally, $Cd_{0.5}Ce^{IV}_2(PO_4)_3$ can be prepared by solid-state reaction at 1373 K (Orlova *et al.*, 2005). The latter compound is isostructural with monazite, with Cd and Ce atoms randomly occupying the same crystallographic site.

We present here the structure determination of a new mixed orthophosphate containing tetravalent cerium, *viz.* $K_4CeZr(PO_4)_4$ (I). The projection of the structure of (I) on to the bc

plane shows the three-dimensional character of the $[CeZr(PO_4)_4]_\infty$ framework (Fig. 1). The structure can be described as a combination of ZrO_6 octahedra, CeO_8 dodecahedra and PO_4 tetrahedra linked together by sharing corners and edges. The rigid framework contains tunnels running along the a and b directions, in which the K^+ cations are located.

A complex disorder involving the phosphate groups is observed in (I). The P-atom positions are split equally over two sites, *viz.* PA (8*e* site, 50% occupancy) and PB (16*h* site, 25% occupancy). The O1 (16*h*) position is fully occupied but the other O atoms are disordered over three sites, *viz.* O2A (16*h*, 50% occupancy), O2B (8*e*, 50% occupancy) and O3 (16*h*, 25% occupancy) (Fig. 2). The disorder appears as a result of the mixed Ce/Zr occupancy and of their different sizes and bonding requirements. Three types of $M-O$ distances are observed in (I): 1.998 (11), 2.141 (4) and 2.491 (6) Å (Table 1). The latter distance is rather long for Zr^{IV} atoms by comparison with $K_2Zr(PO_4)_2$, which has $Zr-O$ distances of 2.060 (6) and 2.072 (3) Å (Doerffel & Liebertz, 1990). In $Cd_{0.5}Ce^{IV}_2(PO_4)_3$ (Orlova *et al.*, 2005), the $Ce-O$

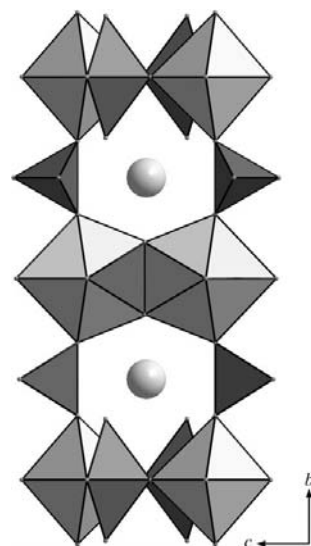


Figure 1

A projection of (I) on to the bc plane. CeO_8 and ZrO_6 polyhedra are shown with light-grey shading, PO_4 tetrahedra with dark-grey shading and K atoms as light-grey circles.

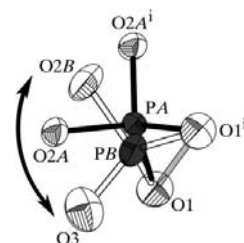


Figure 2

A view of the disorder in the PO_4 tetrahedron (50% probability displacement ellipsoids). [Symmetry code: (i) $-x, -y + \frac{3}{2}, z$.]

distances are in the range 2.40 (1)–2.87 (1) Å for nine-coordinated Ce^{IV} atoms.

Four phosphate groups coordinate the M ($= \text{Ce}$ or Zr) atom *via* O1 atoms, forming an equatorial square-planar arrangement with $M\text{—O1}$ distances of 2.141 (4) Å. For $M = \text{Ce}$, the coordination is completed by four O2A atoms (Fig. 3a). A similar oxygen environment can be found for Zr in ZrSiO_4 (Siggel & Jansen, 1990). For $M = \text{Zr}$, the coordination is completed by two O2B atoms (Fig. 3b). Thus, Ce is eight-coordinated and Zr is six-coordinated. The O2B and O3 positions result from a rotation of 32.3 (6)° of the PO_4 tetrahedron around the O1–O1' edge (symmetry code as in Fig. 2). Bond-valence-sum (BVS) calculations confirm the six- and eightfold coordinations of the Zr and Ce atoms, respectively. The BVS around Zr is 4.00 (4 Zr1–O1 bonds with $\text{BV} = 0.576$ and 2 Zr1–O2B bonds with $\text{BV} = 0.848$), while the BVS around Ce is 4.09 (4 Ce1–O1 bonds with $\text{BV} = 0.737$ and 4 Ce1–O2A bonds with $\text{BV} = 0.286$) (Brese & O'Keeffe, 1991; Brown, 2002).

The potassium cations are located in tunnels running in two orthogonal directions parallel to the a and b axes, with diameters of approximately 4 Å. Their oxygen environment depends on the orientation of the disordered PO_4 group, which yields a wide range of K–O distances (2.532–3.087 Å). The BVS calculation gives a value of 1.1, taking into account the partial occupancies of the O sites. The K^+ ions are at a distance of 3.3520 (6) Å from one another and ionic conductivity may be expected on the basis of the large tunnel dimensions.

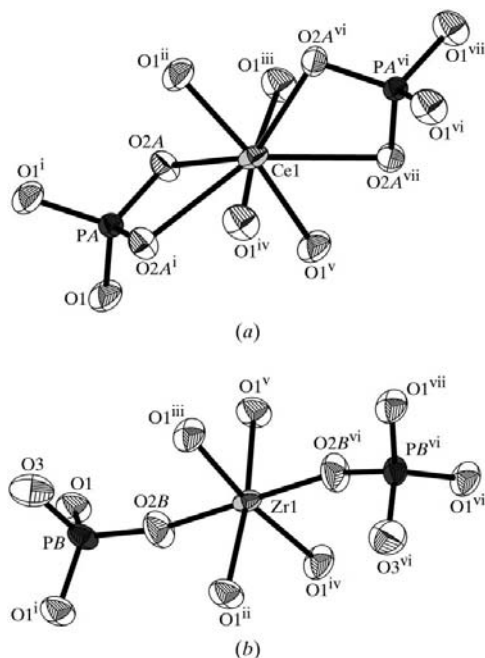


Figure 3

The O-atom environment and structural arrangement around (a) the Ce1 and (b) the Zr1 atom (50% probability displacement ellipsoids). [Symmetry codes: (i) $-x, -y + \frac{3}{2}, z$; (ii) $-x, y + \frac{1}{2}, -z + 1$; (iii) $y - \frac{1}{4}, -x + \frac{3}{4}, z + \frac{1}{4}$; (iv) $-y + \frac{1}{4}, x + \frac{3}{4}, z + \frac{1}{4}$; (v) $x, -y + 1, -z + 1$; (vi) $y - \frac{3}{4}, x + \frac{3}{4}, -z + \frac{5}{4}$; (vii) $-y + \frac{3}{4}, -x + \frac{3}{4}, -z + \frac{5}{4}$.]

Experimental

The title compound can be obtained easily using the self-flux technique in air. However, ZrO_2 has low solubility in phosphate fluxes and ZrF_4 was used as a starting Zr compound. CeF_3 was used for the same reason. In a first step, a mixture of KPO_3 (4.52 g) and $\text{K}_4\text{P}_2\text{O}_7$ (3.4 g) was melted in a platinum crucible at 1273 K for 1 h with stirring. The mixture was then cooled quickly to 1173 K and a ground mixture of ZrF_4 (0.84 g) and CeF_3 (1.05 g) was added. The temperature of the crucible was kept constant for 30 min and then cooled at a rate of 25 K h^{-1} to 913 K, and the molten glass was poured out. After cooling to room temperature and rinsing in hot deionized water, a mixture of yellow crystals of (I) (0.1–0.15 mm in size) and CePO_4 powder was recovered. This mixture was separated by sedimentation in water. Crystals of (I) were dried at 400 K in air and sieved. The purity of (I) was checked using powder X-ray diffraction (DRON-3 Ni-filtered $\text{Cu K}\alpha$ radiation). CePO_4 and other crystalline impurities were not detected. The ICP determination of K, Ce and Zr in (I) yielded an atomic ratio of the elements of 3.95:0.97:0.98. Further analysis for K, Ce, Zr and P was performed by energy dispersive spectroscopy; the analysis yielded atomic ratios equal to 3.9:1.05:1.03:4. In order to check for the presence of fluorine, the sample was melted with NaOH at 800 K in a gold crucible and washed with hot deionized water. Nitric acid was then added to the crucible. Fluoride ions were precipitated as PbClF and the chloride content was estimated by Volhard's method, from which the fluoride content was calculated (Vogel, 1962). No fluorine was detected in (I). By the same technique, we also synthesized $\text{K}_4\text{CeHf}(\text{PO}_4)_4$, but with smaller crystal dimensions (unpublished work).

Crystal data

$\text{K}_4\text{CeZr}(\text{PO}_4)_4$
 $M_r = 767.62$
 Tetragonal, $I4_1/amd$
 $a = 6.7039$ (9) Å
 $c = 17.065$ (3) Å
 $V = 766.9$ (2) Å³
 $Z = 2$

$D_x = 3.330 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 5.24 \text{ mm}^{-1}$
 $T = 293$ (2) K
 Tetragonal bipyramid, light yellow
 $0.16 \times 0.13 \times 0.12 \text{ mm}$

Data collection

Oxford Diffraction XCalibur-3
 diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (Blessing, 1995)
 $T_{\min} = 0.442$, $T_{\max} = 0.501$
 (expected range = 0.471–0.533)

3037 measured reflections
 327 independent reflections
 292 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.034$
 $\theta_{\max} = 30.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.029$
 $wR(F^2) = 0.080$
 $S = 1.03$
 327 reflections
 41 parameters

$w = 1/[\sigma^2(F_o^2) + (0.062P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.59 \text{ e Å}^{-3}$
 $\Delta\rho_{\min} = -0.86 \text{ e Å}^{-3}$

The Ce and Zr atomic coordinates and displacement parameters were constrained and their occupancies were refined. After the final refinement cycles, the P and O atoms were found to have high U_{eq} values and the convergence factors were also high. Three peaks were assigned as extra P- and O-atom positions according to the anion geometry. The occupancies of the P and O sites were calculated from the compound stoichiometry and fixed.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2005); program(s) used to solve structure: *SIR2004*

Table 1

Selected geometric parameters (Å, °).

Ce1—O1 ^{viii}	2.141 (4)	K1—O1	3.087 (3)
Ce1—O2A	2.491 (6)	K1—K1 ⁱ	3.3520 (6)
Zr1—O2B	1.998 (11)	PA—O2A	1.529 (8)
Zr1—O1 ^{viii}	2.141 (4)	PA—O1	1.561 (7)
K1—O3 ^{ix}	2.532 (14)	PB—O1	1.464 (8)
K1—O2A ^{ix}	2.729 (5)	PB—O2B	1.488 (14)
K1—O3	2.930 (19)	PB—O3	1.59 (2)
O2A—PA—O2A ⁱ	103.3 (7)	O1—PB—O2B	111.3 (4)
O2A—PA—O1	112.88 (14)	O1—PB—O3	106.0 (5)
O1—PA—O1 ⁱ	102.4 (6)	O2B—PB—O3	109.4 (11)
O1—PB—O1 ⁱ	112.5 (8)		

Symmetry codes: (i) $-x, -y + \frac{3}{2}, z$; (viii) $-x, -y + 1, -z + 1$; (ix) $-y + \frac{5}{4}, -x + \frac{5}{4}, -z + \frac{3}{4}$.

(Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC3019). Services for accessing these data are described at the back of the journal.

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