Crystal structure of a lithium-filled langbeinite variant, $Li(H_2O)_2[Hf_2(PO_4)_3]$

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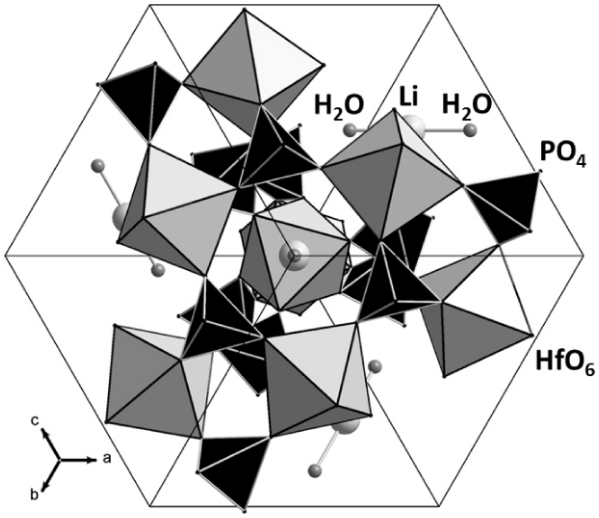

Abstract

$H_4Hf_2LiO_{14}P_3$, cubic, $P2_13$ (no. 198), a = 10.1993(2) Å, V = 1061.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.022, $wR_{ref}(F^2)$ = 0.035, T = 295 K.

Source of material

$HfCl_4$ (0.320 g, 1 mmol, Alfa, 99.5 %), $Li_2B_4O_7$ (0.324 g, 2 mmol, Sigma-Aldrich, 98 %), 0.1 mL H_3PO_4 (Carl Roth, 85 wt %, p.a.) and water (5.0 mL) were mixed (constant stirring) and transferred to a 20 mL Teflon-lined autoclave. The pH value was adjusted to 1 via addition of diluted (~10 wt %) HCl (Merck, 37 wt %, p.a.). After a reaction time of 8 days (autogenous pressure at 180 °C), colorless crystals were isolated as single phase product after filtration and washing with water. Based on Hf, the yield is estimated to be ~50 wt %.

Experimental details

Hydrogen atoms (localized from difference Fourier maps) were included with partial occupancies in the final steps of refinement. The lattice parameters were obtained by least-squares fitting of a total of 80 reflections extracted from the X-ray powder pattern (Cu Kα_1 radiation, λ = 1.54060 Å, 10° < 2θ < 120°).

Discussion

The title compound is an isotype of $Li(H_2O)_2[Zr_2(PO_4)_3]$ [1]. $Li(H_2O)_2[Hf_2(PO_4)_3]$ owns the framework of langbeinite which consists of HfO_6 octahedra and PO_4 tetrahedra linked to each other by sharing common oxygen atoms. There are two crystallographically different Hf^{4+} ions which are both six-fold coordinated by oxygen atoms. The Hf1 octahedron is slightly distorted with Hf1—O distances of 3 × 2.030(3) Å and 3 × 2.074(3) Å, while in the Hf2 octahedron Hf2—O distances are almost equal: 3 × 2.060(3) Å and 3 × 2.067(3) Å. P—O bond lengths within the phosphate tetrahedron vary from 1.521(3) Å to 1.532(3) Å with an average distance of 1.528 Å which is in accordance with the expectation for a non-protonated phosphate group [2]. The alternating HfO_6 octahedra and PO_4 tetrahedra form enlongated cages which are filled with one Li^+ ion and two crystal water molecules (situated on the three-fold axis). A linear coordination of Li by two water molecules is observed with d(Li—O5W) = 1.80(3) Å and d(Li—O6W) = 1.85(3) Å, respectively. Six oxygen atoms of the framework complete the [2 + 6] coodination sphere of Li (d(O—Li) = 3 × 2.517(3) Å and 3 × 2.663(5) Å). The lattice parameter (a = 10.1993(2) Å) for the Hf compound is slightly smaller than the one for $Li(H_2O)_2[Zr_2(PO_4)_3]$ (a = 10.2417(1) Å) [1] which is in general accordance with the ionic radii: Hf^{4+} (r = 0.71 Å), Zr^{4+} (r = 0.72 Å) [3].

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.02 × 0.02 × 0.02 mm
Wavelength:	Ag K_α radiation (0.56089 Å)
μ:	108.12 cm^{-1}
Diffractometer, scan mode:	Rigaku R-axis Spider 1/4-circle diffractometer, profile data from ω-scans
$2\theta_{max}$:	55.94°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7109, 1739
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1609
$N(param)_{refined}$:	68
Programs:	WinCSD [4], SIR92 [5], SHELXL-97 [6], WinGX [7], Diamond [8]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{iso}
H(51)	12b	0.67	0.575(9)	–0.001(8)	0.04(1)	0.037
H(61)	12b	0.67	0.796(9)	–0.245(8)	0.337(8)	0.036

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hf(1)	4*a*	0.85990(1)	½–x	1–x	0.00734(5)	U_{11}	U_{11}	–0.00015(5)	$-U_{12}$	$-U_{12}$
Hf(2)	4*a*	0.58738(1)	½–x	1–x	0.00663(5)	U_{11}	U_{11}	–0.00032(5)	$-U_{12}$	$-U_{12}$
P(1)	12*b*	0.87519(9)	0.04208(9)	0.22972(9)	0.0080(4)	0.0074(4)	0.0072(4)	0.0011(3)	0.0009(3)	–0.0002(3)
O(1)	12*b*	0.9158(3)	0.1864(3)	0.2303(3)	0.015(1)	0.009(1)	0.016(1)	–0.001(1)	–0.004(1)	0.0013(9)
O(2)	12*b*	0.9617(3)	0.2982(3)	–0.0194(3)	0.017(1)	0.019(1)	0.010(1)	0.003(1)	0.006(1)	–0.003(1)
O(3)	12*b*	0.8566(3)	–0.0076(3)	0.0895(3)	0.019(1)	0.018(1)	0.009(1)	0.002(1)	–0.001(1)	–0.006(1)
O(4)	12*b*	0.7458(3)	0.0233(3)	0.3037(3)	0.011(1)	0.017(1)	0.015(1)	0.001(1)	0.005(1)	–0.000(1)
O(5)	4*a*	0.5721(4)	½–x	x–½	0.031(1)	U_{11}	U_{11}	0.005(2)	$-U_{12}$	U_{12}
O(6)	4*a*	0.7783(4)	½–x	x–½	0.030(2)	U_{11}	U_{11}	–0.001(2)	$-U_{12}$	U_{12}
Li(1)	4*a*	0.674(2)	½–x	x–½	0.13(2)	U_{11}	U_{11}	0.05(1)	$-U_{12}$	U_{12}

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