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The langbeinite-type barium vanadium(III) orthophosphate, $Ba_3V_4(PO_4)_6$

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(P–O) = 0.004 Å
Disorder in solvent or counterion
R factor = 0.027
wR factor = 0.059
Data-to-parameter ratio = 15.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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Langbeinite-type $Ba_3V_4(PO_4)_6$ has been crystallized from a stoichiometric melt starting from $Ba(PO_3)_2$ and V_2O_3. The crystal structure has been refined from single-crystal X-ray diffraction data. It consists of a vanadato(III)–phosphate network $[V_4(PO_4)_6]^{6-}$, which shows some resemblance to the NASICON structure type. A new method is presented for the visualization of this structural relationship. The single-crystal electronic spectrum of yellow–green $Ba_3V_4(PO_4)_6$ shows the absorption bands typical for the octahedral chromophore $[V^{III}O_6]$.

Comment

Quaternary diphosphates $AM^{II}P_2O_7$ (*A*: Ca, Sr, Ba; M^{II}: Mg, Cr–Zn) allow stabilization of transition metals in compara-

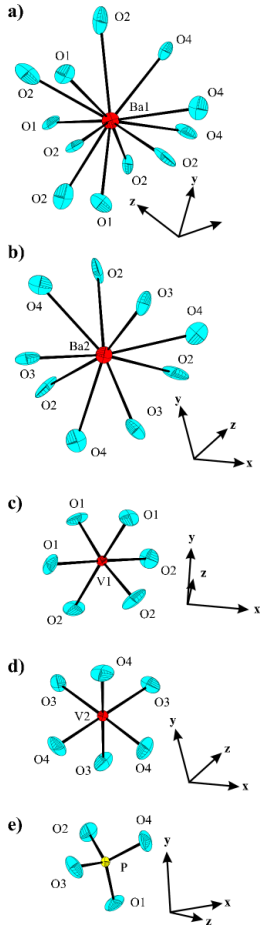

Figure 1
Coordination polyhedra (*a*) [Ba1O_{12}], (*b*) [Ba2O_9], (*c*) [V1O_6], (*d*) [V2O_6] and (*e*) [PO_4], showing displacement ellipsoids at the 74% probability level and the atom numbering.

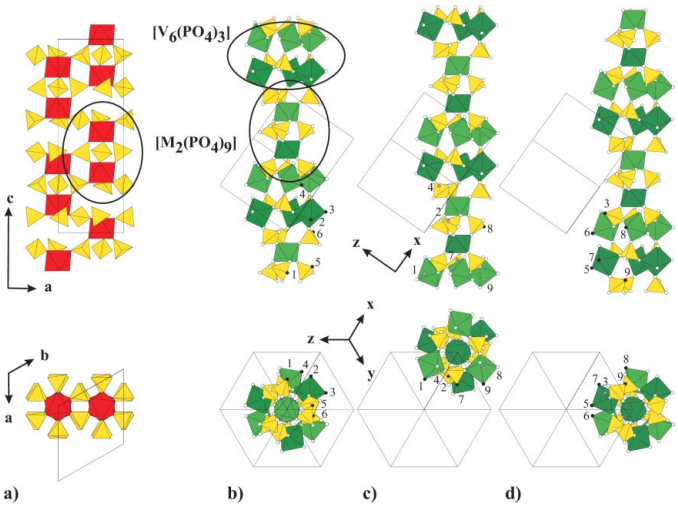

Figure 2
Comparison of the NASICON structure (*a*) with the langbeinite-type structure (*b*)–(*d*) of $Ba_3V_4(PO_4)_6$. Filled numbered dots mark O atoms (in front of the illustration) linking adjacent columns. Building units $[M_2(PO_4)_9]$ (M = Zr, V) and $[V_6(PO_4)_3]$ are highlighted. Colour key: grey shaded dots represent eclipsed oxygen links; red: $[MO_6]$ groups in the NASICON structure; light green: $[V1O_6]$; dark green: $[V2O_6]$; yellow: $[PO_4]$.

tively low oxidation states [*e.g.* Cr^{2+}: $CaCrP_2O_7$ (Maaß *et al.*, 2001), $SrCrP_2O_7$ (Maaß & Glaum, 2000), $BaCrP_2O_7$ (Maaß *et al.*, 2001); Fe^{2+}: $CaFeP_2O_7$ (Maaß, 2002), $SrFeP_2O_7$ (le Meins & Courbion, 1999), $BaFeP_2O_7$ (Maaß, 2002)]. See El Bali *et al.* (2001) and Maaß (2002) for a complete survey of the $AM^{II}P_2O_7$ family.

Aiming at the synthesis of $BaV^{II}P_2O_7$, we obtained $Ba_3V_4(PO_4)_6$. This quaternary orthophosphate belongs to the large langbeinite (Zemann & Zemann, 1957) structure family. In addition to several sulfates (Speer & Salje, 1986; Moriyoshi & Itoh, 1996; Guelylah, Breczewski & Madariaga, 1996; Guelylah, Madariaga & Breczewski, 1996), many phosphates $A_2M_2(PO_4)_3$ (A: alkali or alkaline earth metal, M: tri- or tetravalent transition metal or rare earth metal) (Battle *et al.*, 1986, 1988; Norberg, 2002; Albina *et al.*, 2003) and one fluoroberyllate $K_2Mn_2(BeF_4)_3$ (Guelylah, Breczewski & Madariaga, 1996) belong to this structure family.

The crystal structure of $Ba_3V_4(PO_4)_6$ might be rationalized as a vanadato(III)–phosphate network $[V_4(PO_4)_6]^{6-}$ with Ba^{2+} ions in interstices for charge balance. Taking into account all O atoms closer to Ba than the nearest cation, 12-fold coordination is observed for Ba1 with a rather irregularly shaped coordination polyhedron, while Ba2 forms nine bonds; in this case, the coordination polyhedron might be described as a triply capped octahedron (Fig. 1). The crystal structure of $Ba_3V_4(PO_4)_6$ is just one of a few examples of a langbeinite-type compound with incomplete occupation of the A sites [compare with $K_{2-x}Ti_2(PO_4)_6$ (Leclaire *et al.*, 1989)].

From our refinement, only a slight preference of Ba^{2+} for site Ba1 over Ba2 could be detected. V^{3+} ions are octahedrally coordinated by oxygen from six phosphate groups. The crystallographic site symmetry of both chromophores $[V^{III}O_6]$ belongs to point group C_3. However, the $[V1O_6]$ octahedra show slightly higher angular distortion, as is generally observed for the M1 coordination in other langbeinite structures (Figs. 1*c* and 1*d*). The $[PO_4]$ groups form almost ideal tetrahedra (Fig. 1*e*). Despite its cubic symmetry, the three-dimensional structure of the langbeinite $[V_4(PO_4)_6]^{6-}$ network is quite difficult to describe. A reasonable approach, which we favour, uses a comparison between the crystal structures of the NASICON $NaZr_2(PO_4)_3$ (space group $R\overline{3}c$) (Hagman & Kierkegaard, 1968) and langbeinite structure types (Fig. 2). Both structures might be regarded as transition metal phosphate frameworks with large low-charged cations occupying interstices. For both frameworks, the transiton metal–phosphate ratio is 2:3. In addition to these formal similarities, anionic building units $[M_2(PO_4)_9]$ (M = Zr^{4+} in NASICON, V^{3+} in the described langbeinite) occur in both structures (Fig. 2).

In projections of the cubic langbeinite structure along and perpendicular to [111], one can recognize columns built from $[VO_6]$ and $[PO_4]$ groups having a translational period of one cube diagonal. Within these columns, anionic $[V_2(PO_4)_9]^{21-}$ building units and cationic $[V_6(PO_4)_3]^{9+}$ units alternate, giving to these columns an overall composition $[V_8(PO_4)_{12}]^{12-}$or $[V_4(PO_4)_6]^{6-}$. Perpendicular to [111], these columns are linked by V—O—P bridges. Relative to the central column, adjacent columns are shifted $\frac{1}{2}$ or $\frac{2}{2}$ of the translational period along [111]. In contrast to the NASICON structure type, the presence of the $[V_6(PO_4)_3]^{9+}$ units in the langbeinite structure allows formation of voids large enough to house cations of much bigger size than Na^+. The electronic spectrum of $Ba_3V_4(PO_4)_6$ shows transitions at 14 100 cm^{-1} ($^3T_{1g} \rightarrow {}^3T_{2g}$) and 21 900 cm^{-1} [$^3T_{1g} \rightarrow {}^3T_{2g}(P)$]. Modelling of the transition energies within the framework of the angular overlap model (Jørgensen *et al.*, 1963; Richardson, 1993; Figgis & Hitchman, 2000) leads to good agreement with the observed transitions [B = 596 cm^{-1}, C/B = 4.8, e_σ(mean) = 7750 cm^{-1}, $e_\pi = \frac{1}{4}e_\sigma$] . The resulting bonding parameters compare well with those of VP_3SiO_{11} (Droß, 2004), $V(PO_3)_3$, $V_4P_6Si_2O_{25}$ and $V_4(P_2O_7)_3$ (Glaum, 1999), which have been derived in earlier studies.

Experimental

Crystals of $Ba_3V_4(PO_4)_6$ were grown by melting a homogenized mixture of $Ba(PO_3)_2$ (150 mg, 0.5071 mmol) and V_2O_3 (50.67 mg, 0.3381 mmol) in a platinum crucible in air. The melt [T_m = 1373 (20) K] was rapidly heated, using an electrical furnace, to 1473 K, kept at that temperature for 1 h, cooled to 1073 K at a rate of 10 K h^{-1} and finaly to room temperature at a rate of 50 K h^{-1}. After removing the crucible from the oven, the recrystallized melt was crushed and crystal fragments of the title compound were obtained. Microcrystalline single-phase powders were obtained from pellets (size 4 × 4 × 12 mm) of the starting materials $Ba(PO_3)_2$ and V_2O_3 after heating for 3 d at 1323 K in sealed silica tubes (L = 10 cm and D = 1.6 cm) in the presence of 30 mg iodine as mineralizer. Subsequent heating for 21 d yielded small yellow–green crystals of irregular shape.

Crystal data

$Ba_3V_4(PO_4)_6$
M_r = 1185.58
Cubic, $P2_13$
a = 9.8825 (7) Å
V = 965.16 (12) Å^3
Z = 2
D_x = 4.08 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 29 reflections
θ = 2.9–30.0°
μ = 8.49 mm^{-1}
T = 293 (2) K
Cube, yellow–green
0.1 × 0.1 × 0.1 mm

Data collection

Nonius KappaCCD diffractometer
ψ and ω scans
Absorption correction: numerical (*HABITUS*; Herrendorf, 1993)
T_{min} = 0.597, T_{max} = 0.707
22 794 measured reflections
930 independent reflections
930 reflections with $I > 2\sigma(I)$
R_{int} = 0.029
θ_{max} = 30.0°
$h = -13 \rightarrow 13$
$k = -13 \rightarrow 13$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.059
S = 1.13
930 reflections
61 parameters
$w = 1/[\sigma^2(F_o^2) + 7.2584P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.015
$\Delta\rho_{max}$ = 2.02 e Å^{-3}
$\Delta\rho_{min}$ = −1.90 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0237 (15)
Absolute structure: Flack (1983), 393 Friedel pairs
Flack parameter = −0.02 (3)

Table 1
Selected geometric parameters (Å, °).

Ba1—O1^{i}	2.843 (4)	V1—O2^{iv}	1.998 (4)
Ba1—O4^{ii}	2.961 (4)	V2—O4^{v}	1.996 (3)
Ba1—O2^{i}	3.047 (5)	V2—O3^{vi}	1.999 (3)
Ba1—O2^{ii}	3.225 (5)	P—O1	1.516 (3)
Ba2—O3	2.824 (4)	P—O4	1.521 (3)
Ba2—O4^{i}	3.009 (4)	P—O2	1.531 (4)
Ba2—O2^{i}	3.111 (4)	P—O3	1.534 (3)
V1—O1^{iii}	1.983 (3)		
O1^{iii}—V1—O1^{vii}	93.73 (16)	O4^{v}—V2—O4^{viii}	88.44 (17)
O1^{iii}—V1—O2^{iv}	81.84 (18)	O4^{v}—V2—O3^{vi}	88.61 (15)
O1^{vii}—V1—O2^{iv}	92.35 (17)	O4^{viii}—V2—O3^{vi}	176.20 (17)
O1—V1—O2^{iv}	172.71 (18)	O4^{ix}—V2—O3^{vi}	89.08 (17)
O2^{iv}—V1—O2^{vi}	92.50 (16)	O3^{vi}—V2—O3^{iv}	93.75 (17)

Symmetry codes: (i) $\frac{1}{2}-z, 1-x, y-\frac{1}{2}$; (ii) $-z, x-\frac{1}{2}, \frac{1}{2}-y$; (iii) z, x, y; (iv) $1-y, \frac{1}{2}+z, \frac{3}{2}-x$; (v) $1-z, \frac{1}{2}+x, \frac{3}{2}-y$; (vi) $\frac{1}{2}+z, \frac{3}{2}-x, 1-y$; (vii) y, z, x; (viii) $\frac{3}{2}-y, 1-z, \frac{1}{2}+x$; (ix) $\frac{1}{2}+x, \frac{3}{2}-y, 1-z$.

The lattice parameters were refined with the program *SOS* (Soose, 1980), using 29 reflections from an image plate Guinier photograph. Site-occupation factors for Ba1 and Ba2 have been refined with and without a restraint on their sum; both results are identical within standard uncertainty [with SUMP: s.o.f.(Ba1) = 0.772 (2), s.o.f.(Ba2) = 0.727 (2); without SUMP: s.o.f.(Ba1) = 0.776 (4), s.o.f.(Ba2) = 0.732 (4)]. The maximum and minimum electron-density peaks are located 0.67 and 0.62 Å, respectively from Ba2..

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *COLLECT* and *DENZO* (Otwinowski & Minor, 1997); data reduction: *COLLECT* and *DENZO*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 2002); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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