inorganic papers

Apatite-type Ba$_5$(VO$_4$)$_3$Cl

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The title compound, pentabarium tris(vanadate) chloride, crystallizes in the well known apatite structure type, with space group $P6_3/m$ and $Z = 2$. The crystal structure contains isolated (VO$_4$)$^{3-}$ tetrahedra that are bridged by Ba^{2+} ions. The intermediate Cl$^-$ anions, situated on positions with $\bar{3}$ symmetry, are octahedrally surrounded by Ba^{2+} cations.

Key indicators

Single-crystal X-ray study
$T = 298$ K
Mean σ(V–O) = 0.004 Å
R factor = 0.015
wR factor = 0.034
Data-to-parameter ratio = 14.2

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

Comment

Single crystals of the title compound were first obtained as an impurity during our attempt to explore new compounds in the Ba–V–Ru–O system, with BaCl$_2$·2H$_2$O used as an excess flux material. Once its composition and preliminary crystal structure were identified by elemental and X-ray diffraction analyses, it was possible to prepare single-phase material of Ba$_5$(VO$_4$)$_3$Cl as both powder and single crystals. To our knowledge, only the cell dimensions and the powder pattern of Ba$_5$(VO$_4$)$_3$Cl have been reported to date (Powder Diffraction File No. 19-0099; ICDD, 2001), without any further details of the crystal structure. Here, we report the synthesis of the compound and its crystal structure, as determined from single-crystal data.

Ba$_5$(VO$_4$)$_3$Cl crystallizes in the well known apatite structure type, like the related compound Sr$_5$(PO$_4$)$_3$Br and its Eu^{2+} doped analogues, which find application as photoluminescent materials (Nötzold & Wulff, 2000). The structure consists of VO$_4^{3-}$ tetrahedra bridged by Ba^{2+} ions, and intermediate Cl$^-$
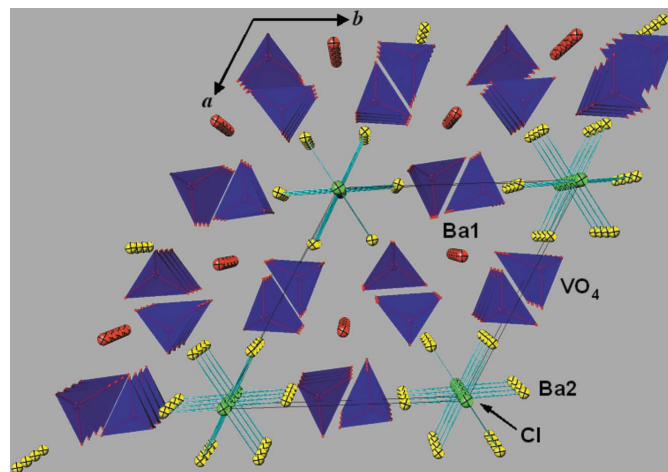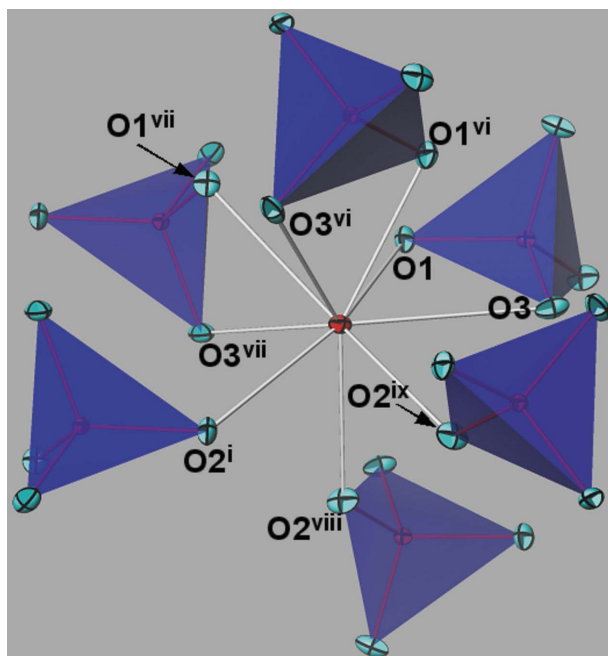

Figure 1
A polyhedral representation of the crystal structure of Ba$_5$(VO$_4$)$_3$Cl, projected on (001). The unit cell is outlined. The V ions are at the centre of blue VO$_4$ tetrahedra. Ba1, Ba2 and Cl ions are drawn as red, yellow and green ellipsoids, respectively, and are scaled at the 90% probability level.

Figure 2
The local environment around Ba1 (red), surrounded by six VO_4 tetrahedra (blue), and coordinated by nine O ions (light blue). All atoms are drawn with 50% probability displacement ellipsoids. [Symmetry codes: (i) y, $1 - x + y$, $-z$ (vi) $y - x$, $1 - x$, z; (vii) $1 - y$, $1 + x - y$, z; (viii) $1 - x$, $1 - y$, $-z$; (ix) $x - y$, x, $z - \frac{1}{2}$.]

Figure 3
The local environment around Ba2 (yellow), coordinated by six O and two Cl atoms. The representation is as in Fig. 2. [Symmetry codes: (iii) y, $y - x$, $\frac{1}{2} + z$; (iv) $y - x$, $1 - x$, z; (x) y, $y - x$, $-z$; (xi) $y - x$, $-x$, $\frac{1}{2} - z$.]
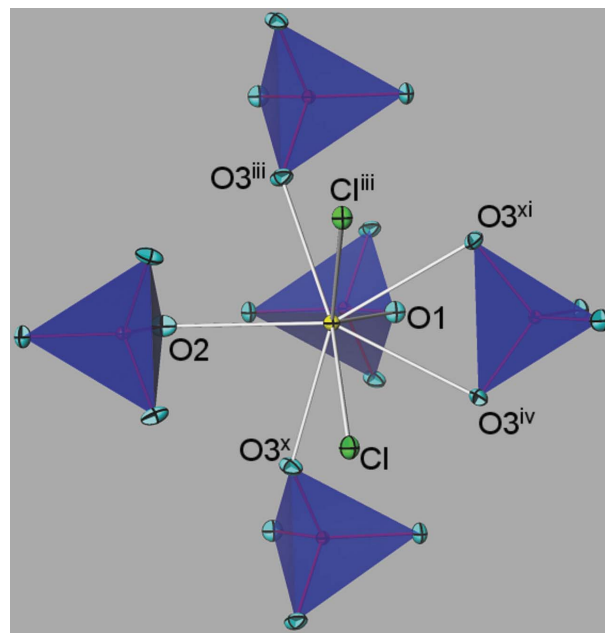
anions. A projection of the crystal structure down the c axis is shown in Fig. 1.

Two crystallographically distinct Ba^{2+} cations are present in the structure. Atom Ba1 is located on a threefold axis and is coordinated to nine O atoms, as shown in Fig. 2. It is connected to six VO_4^{3-} tetrahedra, three of which chelate to the Ba1 cation. Atom Ba2 is coordinated by six O atoms and two Cl atoms. It bridges five VO_4^{3-} tetrahedra, one of which has also chelating character (Fig. 3). The Cl^- anion has site symmetry $\bar{3}$ and is coordinated by six Ba2 atoms. The resultant $[ClBa_6]$ octahedron shows a slight angular distortion.

The empirical expression for bond valence, which has been widely adopted to estimate valences in inorganic solids (Brown, 2002), was used to check the $Ba_5(VO_4)_3Cl$ crystal structure. The bond-valence sums (Brown & Altermatt, 1985; Brese & O'Keeffe, 1991) for atoms Ba1, Ba2, V, Cl, O1, O2 and O3 are 2.15, 2.08, 5.09, 1.18, 2.24, 1.98 and 1.99 v.u., respectively, and these match the expected charges of the ions reasonably well. All interatomic distances (Table 1) are within the expected ranges.

Experimental

$Ba_5(VO_4)_3Cl$ powder was prepared from a mixture of high-purity $BaCO_3$, V_2O_5 and $BaCl_2 \cdot 2H_2O$ in the stoichiometric ratio of 9:3:1. The powder was mixed in an agate mortar, pressed into pellets and then placed in an alumina boat. It was heated twice at 1173 K for 12 h with intermittent mixing and pressing, and finally cooled to room temperature. The heating and cooling rates were 200 K h^{-1}. No other

phases were observed in the powder X-ray diffraction pattern of the light-yellowish product. Single crystals were obtained from a mixture of $Ba_5(VO_4)_3Cl$ powder and $BaCl_2 \cdot 2H_2O$ with a weight ratio of 1:2, heated at 1373 K for 12 h in an alumina crucible, cooled slowly to 1073 K at a rate of 6.25 K h^{-1}, and finally cooled to room temperature at 200 K h^{-1}. The remaining $BaCl_2$ was washed out from the resultant product with distilled water, yielding transparent single crystals of $Ba_5(VO_4)_3Cl$.

Crystal data

$Ba_5(VO_4)_3Cl$	Mo $K\alpha$ radiation
$M_r = 1066.92$	Cell parameters from 526
Hexagonal, $P6_3/m$	reflections
$a = 10.5565$ (1) Å	$\theta = 7.5–70°$
$c = 7.7584$ (1) Å	$\mu = 14.94$ mm^{-1}
$V = 748.76$ (1) Å^3	$T = 298$ K
$Z = 2$	Polyhedron, colourless
$D_x = 4.732$ Mg m^{-3}	$0.15 \times 0.12 \times 0.10$ mm

Data collection

Bruker SMART APEX-2	661 independent reflections
diffractometer	567 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.04$
Absorption correction: multi-scan	$\theta_{max} = 28.2°$
(*SADABS*; Bruker, 2002)	$h = -13 \rightarrow 10$
$T_{min} = 0.17$, $T_{max} = 0.22$	$k = -13 \rightarrow 9$
3252 measured reflections	$l = -10 \rightarrow 5$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.015$	$\Delta\rho_{max} = 0.68$ e Å^{-3}
$wR(F^2) = 0.034$	$\Delta\rho_{min} = -0.52$ e Å^{-3}
$S = 0.46$	Extinction correction: Larson
567 reflections	(1970)
40 parameters	Extinction coefficient: 76.8 (16)
Method of quasi-unit weights,	
$w = [1/(2F_o)]^2$	

Table 1
Selected geometric parameters (Å, °).

Ba1—O1	2.751 (3)	Ba2—O2	2.974 (5)
Ba1—O2^i	2.733 (3)	Ba2—Cl1	3.2878 (3)
Ba1—O3	3.045 (3)	V1—O3	1.698 (3)
Ba2—O1^{ii}	2.603 (4)	V1—O2	1.722 (4)
Ba2—O3^{iii}	2.699 (3)	V1—O1	1.723 (4)
Ba2—O3^{iv}	2.838 (3)		
O3—V1—O3^v	106.2 (2)	O3—V1—O1	106.78 (14)
O3—V1—O2	111.95 (14)	O2—V1—O1	112.8 (2)

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

Cell parameters were refined from powder data collected between 15 and 140° in 2θ [526 data points; Cu Kα_1 radiation (1.5405 Å)]. The LeBail fit method was applied using the *TOPAS* program (Bruker, 2002).

Data collection: *SMART* (Bruker, 2002); cell refinement: *TOPAS* (Bruker, 2002); data reduction: *SAINT* (Bruker, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); mole-cular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *CRYSTALS*.

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