Lanthanum Orthovanadate

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Abstract. LaVO$_4$, monoclinic, $P2_1/n$ (a nonstandard setting of $P2_1/c$, No. 14); $a = 7.047$ (1), $b = 7.286$ (1), $c = 6.725$ (1) Å, $\beta = 104.85$ (1)°; $Z = 4$, $D_{calc} = 5.05$, $D_{obs} = 5.0$ (2) g cm^{-3}. Crystals were grown from a V$_2$O$_5$ flux. The compound is isostructural with monazite (CePO$_4$) with approximate tetrahedral coordination about the vanadium [V–O 1.693 (3) to 1.724 (3) Å] and with the lanthanum coordinated by nine oxygen atoms [La–O 2.497 (3) to 2.886 (3) Å].

Introduction. Crystals were grown by cooling a 5:1 mixture (mole ratio) of V$_2$O$_5$ and La$_2$O$_3$ from 800 °C to room temperature with a cooling rate of approximately 50° h^{-1}. Excess V$_2$O$_5$ was dissolved with aqueous alkali. The resulting crystals of lanthanum orthovanadate were colorless, nearly spherical multifaceted polyhedra up to 0.5 mm in diameter. No attempt was made to optimize conditions in order to increase crystal size.

A small, approximately spherical crystal of diameter 0.06 mm was chosen for data collection. Equi-inclination Weissenberg photographs showed the systematic absences 0k0, $k \neq 2n$ and h0l, $h + l \neq 2n$, establishing the space group as $P2_1/n$.

Intensity data were collected using a computer-controlled CAD-4 diffractometer, employing graphite-monochromated Mo $K\alpha$ radiation. The method of data collection has been described elsewhere (Robinson, 1974). 2011 reflections from a hemisphere of reciprocal space were collected with $3° \leq \theta \leq 30°$, of which 1844 had intensities with $I > \sigma I$. After application of Lorentz, polarization and spherical absorption corrections ($\mu R = 0.49$), equivalent reflections were averaged together to give 971 unique observations. Reflections with $I < \sigma I$ were set equal to $0.5\sigma I$ and included in the refinement.

Lanthanum and vanadium atoms were located on a three-dimensional Patterson map; these atoms were used to phase an F_o map, from which all oxygen atoms were located. The structure was refined by full-matrix least squares using the program RFINE2 of Finger (1972) where $\sum w(\Delta F)^2$ is minimized. With anisotropic temperature factors and an isotropic extinction correction of the form $F_{corr}^2 = F_o^2(1 - sF_o^2)$, the weighted residual $R = \sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2$ was 3.2%; rejection of two very strong reflections (120 and 200) with $|F_o - F_c| > 20$ brought R to 2.4%. The unweighted R was 2.7%. The final value of s was 3.10 (9) $\times 10^{-5}$. The standard deviation of an observation of unit weight was 1.54 with weights taken as $w = 1/\sigma^2 = 4F_o^2/\sigma^2(F_o^2)$.

Positional parameters and temperature factors are shown in Table 1, interatomic distances and angles in Table 2.*
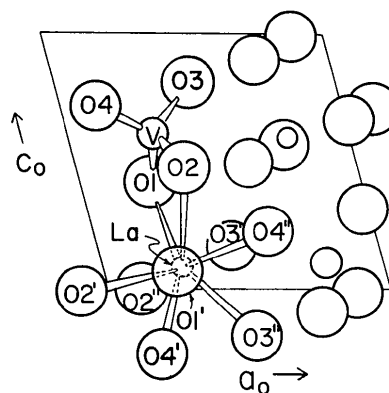

Fig. 1. A projection of the oxygen atoms nearest the La and V atoms in $\frac{1}{4}$ of the unit cell.

Table 1. *Positional and thermal parameters for* LaVO$_4$

All values $\times 10^4$. $f = f_o \exp\left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\right]$. Standard deviations are in parentheses.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
La	2763.3 (3)	1572.5 (3)	1036.4 (4)	32.5 (5)	23.8 (5)	32.9 (6)	0.5 (3)	8.4 (4)	4.2 (4)
V	3005.5 (10)	1646.5 (9)	6149.4 (11)	29.6 (12)	22.6 (10)	24.4 (14)	-1.0 (9)	10.8 (10)	-0.6 (10)
O(1)	2435 (4)	-13 (4)	4263 (5)	64 (6)	34 (5)	62 (7)	-10 (4)	26 (5)	-10 (5)
O(2)	3864 (4)	3434 (4)	4954 (5)	57 (6)	42 (5)	74 (7)	-4 (4)	27 (5)	-14 (5)
O(3)	4815 (5)	1056 (4)	8239 (5)	68 (6)	53 (5)	54 (7)	14 (5)	2 (5)	-12 (5)
O(4)	1180 (5)	2203 (4)	7272 (5)	51 (6)	61 (5)	55 (7)	2 (4)	16 (5)	-7 (5)

Discussion. Of the rare earth orthovanadates, only $LaVO_4$ crystallizes in the AXO_4 monazite structure isomorphous with monoclinic $LaPO_4$ and $CePO_4$ (Wyckoff, 1965). This is a somewhat flexible structure containing approximately tetrahedral XO_4 units and a very irregular coordination polyhedron about A. The coordination number about A varies from structure to structure and there are wide variations of the A–O distances within a given polyhedron.

Pertinent bond distance and angle data for $LaVO_4$ are shown in Table 2. In a previous determination of the $LaVO_4$ structure, Brusset, Maduale-Aubry, Mahé & Boursier (1971) reported the lanthanum atom to be coordinated by eight oxygens at distances of 2·22 to 2·95 Å. Our work shows La to be nine coordinate with more realistic La–O distances of 2·497 (3) to 2·886 (3) Å. The coordination polyhedron about La is not regular, but can be visualized as an irregular pentagon with two additional oxygen atoms above and two oxygen atoms below the plane of the pentagon. Fig. 1 shows this polyhedron viewed almost parallel to the pentagonal plane. The distances are typical of those found in many La oxides and complex oxides. The coordination about vanadium is roughly tetrahedral; the average V–O bond distance of 1·709 Å is typical of metal orthovanadates.

Table 2. *Distances and angles in* $LaVO_4$

(a) Distances (Å)

V–O(1)	x,	y,	z^*	1·724 (3)
–O(2)	x,	y,	z	1·720 (3)
–O(3)	x,	y,	z	1·693 (3)
–O(4)	x,	y,	z	1·699 (3)
La–O(1)	x,	y,	z	2·520 (3)
–O(1)′	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$			2·497 (3)
–O(2)	x,	y,	z	2·886 (3)
–O(2)′	$x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$			2·657 (3)
–O(2)″	$\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$			2·569 (3)
–O(3)′	$1-x, -y, 1-z$			2·528 (3)
–O(3)″	x,	y,	$z-1$	2·677 (3)
–O(4)′	x,	y,	$z-1$	2·533 (3)
–O(4)″	$x+\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$			2·502 (3)

* x,y,z refers to oxygen positions in Table 1.

Table 2 *(cont.)*

(b) Bond angles (°)

O(1)—V—O(2)	103·32 (15)
O(1)—V—O(3)	114·62 (15)
O(1)—V—O(4)	115·72 (15)
O(2)—V—O(3)	107·46 (16)
O(2)—V—O(4)	115·11 (15)
O(3)—V—O(4)	100·78 (16)
O(1)—La–O(1)′	120·68 (8)
O(1)—La–O(2)	59·48 (9)
O(1)—La–O(2)′	85·32 (10)
O(1)—La–O(2)″	71·44 (10)
O(1)—La–O(3)′	72·15 (10)
O(1)—La–O(3)″	136·53 (9)
O(1)—La–O(4)′	146·02 (10)
O(1)—La–O(4)″	99·82 (10)
O(1)′–La–O(2)	66·54 (9)
O(1)′–La–O(2)′	86·96 (9)
O(1)′–La–O(2)″	148·67 (10)
O(1)′–La–O(3)′	142·30 (10)
O(1)′–La–O(3)″	96·47 (10)
O(1)′–La–O(4)′	74·79 (11)
O(1)′–La–O(4)″	72·59 (10)
O(2)—La–O(2)′	105·55 (10)
O(2)—La–O(2)″	130·73 (7)
O(2)—La–O(3)′	99·77 (9)
O(2)—La–O(3)″	129·80 (9)
O(2)—La–O(4)′	140·65 (9)
O(2)—La–O(4)″	61·23 (9)
O(2)′–La–O(2)″	64·25 (11)
O(2)′–La–O(3)′	130·65 (10)
O(2)′–La–O(3)″	120·96 (10)
O(2)′–La–O(4)′	64·32 (10)
O(2)′–La–O(4)″	158·70 (10)
O(2)″–La–O(3)′	67·05 (10)
O(2)″–La–O(3)″	88·76 (10)
O(2)″–La–O(4)′	81·34 (10)
O(2)″–La–O(4)″	137·00 (10)
O(3)′–La–O(3)″	64·48 (12)
O(3)′–La–O(4)′	115·64 (11)
O(3)′–La–O(4)″	70·20 (10)
O(3)″–La–O(4)′	60·15 (10)
O(3)″–La–O(4)″	68·66 (10)
O(4)′–La–O(4)″	114·03 (11)

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