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BRIEF COMMUNICATION

$LaNb_2O_6Cl$: A New Lanthanum Halo Niobate

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$LaNb_2O_6Cl$ has been prepared by the interaction of LaOCl and Nb_2O_5. It crystallizes in the orthorhombic space group *Pnma* with $a = 9.752$, $b = 7.306$, $c = 8.365$ Å, and the structure was refined to an R value of 1.9%. The most unusual feature of the structure is the participation of one Cl atom in the octahedral environment of Nb(2) combined with one short Nb–O distance.

We have recently reported on the structure of rare earth halo tungstates, where W is only coordinated to oxygen. In $La_3WO_6Cl_3$ (*1*), the tungsten has trigonally prismatic six coordination, while in $LaWO_4Cl$ (*2*) it is five coordinated in the form of a trigonal bipyramid, and in $GdWO_4Cl$ (*3*) it is tetrahedral. Similar compounds also exist for molybdenum, but it appears that no such compositions are described for niobium. Therefore, we prepared the first halo niobate of lanthanum and determined its structure in detail.

Experimental and Results

A. Preparation

$LaNb_2O_6Cl$ was prepared from the components LaOCl and Nb_2O_5 in an evacuated quartz tube. LaOCl was made by dissolving high purity La_2O_3 (99.99% purity, Research Chemical Corp.) in HCl, taking the solution to dryness, and firing the resulting product at 900°C in air for 6–10 hr. Nb_2O_5 obtained from the supplier (optical grade Kawecki/Berylco) was fired at 1000°C for 1–2 hr in air before use. The stoichiometric quantities (totaling less than 10.000 g) of LaOCl and Nb_2O_5 were sealed into the (1-cm-diameter, 20-cm-long) quartz tube and fired at 900°C for 8–12 hr. When the tube was opened, HCl could be detected, suggesting that despite the careful drying and firing of the components, trace quantities of H_2O must have been released from the chemicals or the reaction tube. It is conceivable that the HCl actually acted as a transport agent and helped in the formation of the pale amber single crystals used for the structure determination. Although powder patterns of material obtained in this manner could be completely indexed, small impurities of unknown composition were observed occasionally.

B. X-Ray Studies

1. Powder examination. The X-ray powder diffraction pattern of $LaNb_2O_6Cl$ was obtained with a focusing camera (radius 40

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TABLE I

POWDER DIFFRACTION DATA FOR $LaNb_2O_6Cl$

I/I_0	h	k	l	d(obs)	d(calc)
60	1	1	0	6.3086	6.3491
5	1	0	1	5.4758	5.5028
30	0	2	0	4.8605	4.8758
5	1	1	1	4.7840	4.7924
60	1	2	0	4.2042	4.2125
20	2	0	0	4.1750	4.1825
15	0	2	1	4.0501	4.0557
40	2	1	0	3.8391	3.8438
65	1	2	1	3.6477	3.6494
	0	0	2		3.6531
30	2	1	1	3.4006	3.4018
100	2	2	0	3.1720	3.1746
100	1	1	2	3.1658	3.1664
75	1	3	0	3.0291	3.0298
100	0	2	2	2.9226	2.9236
20	2	2	1	2.9126	2.9116
20	1	2	2	2.7585	2.7599
95	2	0	2	2.7515	2.7514
45	3	1	0	2.6815	2.6809
25	2	1	2	2.6483	2.6480
15	3	0	1	2.6054	2.6051
30	2	3	0	2.5672	2.5666
45	3	1	1	2.5175	2.5168
15	0	4	0	2.4392	2.4379
80	2	3	1	2.4216	2.4215
	3	2	0		2.4205
30	2	2	2	2.3967	2.3962
40	1	4	0	2.3403	2.3406
	1	0	3		2.3383
	1	3	2		2.3321
30	0	4	1	2.3130	2.3126
5	1	1	3	2.2745	2.2739
30	1	4	1	2.2298	2.2290
15	0	2	3	2.1797	2.1788

mm) of Guinier—Hägg type. The radiation was monochromatic Cu$K\alpha$, (λ = 1.5405 Å), and Si (a = 5.4305 Å) was used as an internal standard. Line positions on the film were determined to ±5 μm with a David Mann film reader (a precision screw, split image comparator). Intensities were estimated by oscilloscopic comparison of film density with the strongest line of the pattern. Refined cell dimensions were obtained by a least squares procedure (local program).

TABLE II

FRACTIONAL COORDINATES (×10000) AND ISOTROPIC THERMAL PARAMETERS

Atom	x	y	z
La(1)	3182.6(4)	7500	3114.9(4)
Nb(1)	5000	5000	0.0
Nb(2)	2653.9(6)	2500	2687.5(6)
Cl(1)	3963(2)	2500	5693(2)
O(1)	1692(5)	2500	910(5)
O(2)	5055(4)	7500	786(5)
O(3)	3960(3)	4453(4)	1992(3)
O(4)	3255(3)	5471(4)	−1136(3)

The indexed powder pattern of $LaNb_2O_6Cl$ is reported in Table I. The refined cell dimensions are

$$a = 9.752(2)\ \text{Å}$$

$$b = 7.306(1)\ \text{Å}$$

$$c = 8.365(1)\ \text{Å}.$$

The figures of merit (*4*, *5*) for this data set are

$$M_{20} = 25$$

$$F_{20} = 35(0.026,22).$$

2. Single crystal work. A crystal with dimensions 0.2 × 0.02 × 0.04 mm was placed on an Enraf-Nonius CAD4 X-ray diffractometer equipped with a graphite monochromated Mo$K\alpha$ source. Preliminary search techniques confirmed the orthorhombic lattice with a = 9.748(3), b = 7.292(2), and c =

TABLE III

ANISOTROPIC THERMAL PARAMETERS (×1000)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
La(1)	9.9(2)	7.9(2)	6.7(2)	—	0.2(1)	—
Nb(1)	6.7(3)	4.2(2)	8.0(2)	−0.1(2)	0.1(2)	−0.6(2)
Nb(2)	7.5(3)	6.9(2)	5.4(2)	—	−0.2(2)	—
Cl(1)	9.4(8)	31.7(8)	10.0(6)	—	−0.9(5)	—
O(1)	12(3)	17(2)	7(2)	—	−2(1)	—
O(2)	13(2)	5(2)	9(2)	—	2(1)	—
O(3)	7(2)	7(1)	7(1)	−3(1)	2(1)	2(1)
O(4)	7(2)	7(1)	9(1)	1(1)	−1(1)	1(1)

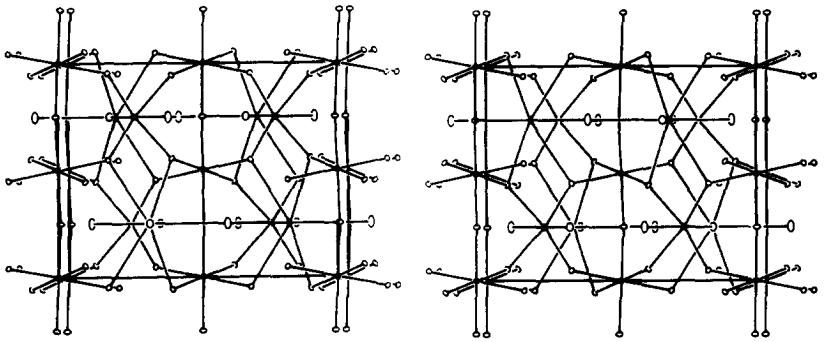

FIG. 1. Stereoscopic view along [001] showing the NbO_6 chains linked by the second NbO_5Cl octahedra and the LaO_6Cl_2.

8.362(2) with systematic absences compatible with *Pnma* (No. 62) or $Pn2_1a$ (No. 33). For $LaNb_2ClO_6$ with $Z = 4$, the calculated density is 5.097 g/cc. A total of 2707 reflections were obtained with the θ–2θ scan made from $4° \leq 2\theta \leq 60°$ with scan range $\omega = 0.7 + 0.35 \tan(\theta)$ and a speed of 2°/min. There was no evidence of intensity fluctuation during the measurement. After the usual preliminary corrections for Lorentz polarization, the data were merged to yield 868 reflections, 768 of which with $I \geq 2\sigma(I)$ were used for structure determination and refinement. The structure of $LaNb_2O_6Cl$ was determined from the heavy atom method using the centric space group *Pnma*. Anisotropic full-matrix least squares refinement converged with $R = 0.019$ and $R_2 = 0.026$. A final difference Fourier map revealed several expected large peaks (0.5–1.2*e*) near the La and oxygen atoms. A refinement of the multiplicity factors for the La, Nb, and Cl atoms revealed full occupancy at these sites. The atomic scattering factors and anomalous dispersion corrections were taken from the International Tables for X-Ray Crystallography, Vol. IV. Refined atom coordinates, thermal parame-

TABLE IV

INTERATOMIC DISTANCES (Å)*

		Nb(1)–O(2)	1.938(1)
La(1)–Cl(1)[a]	2.956(2)	Nb(1)–O(3)	1.990(3)
La(1)–Cl(1)[b]	2.911(2)	Nb(1)–O(4)	1.978(3)
La(1)–O(1)[c]	2.340(4)	Nb(2)–Cl(1)	2.819(2)
La(1)–O(2)	2.669(4)	Nb(2)–O(1)	1.757(4)
La(1)–O(3)	2.529(3)	Nb(2)–O(3)	1.997(3)
La(1)–O(4)[c]	2.655(3)	Nb(2)–O(4)[d]	1.986(3)

* The subscripts *a*, *b*, *c*, *d* refer to equivalent symmetry operators, respectively: (a) $-x, -y, 1 - z$; (b) $-\frac{1}{2} - x, \frac{1}{2} + y, -\frac{1}{2} + z$; (c) $-\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$; (d) $-\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} + z$.

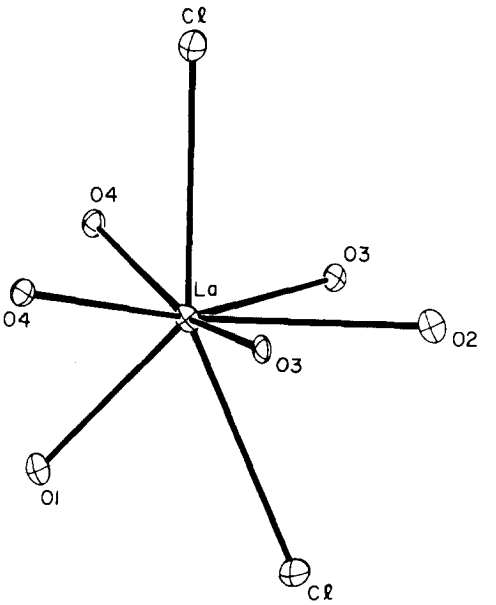

FIG. 2. Coordination sphere of LaO_6Cl_2 shown at 50% thermal ellipsoids.

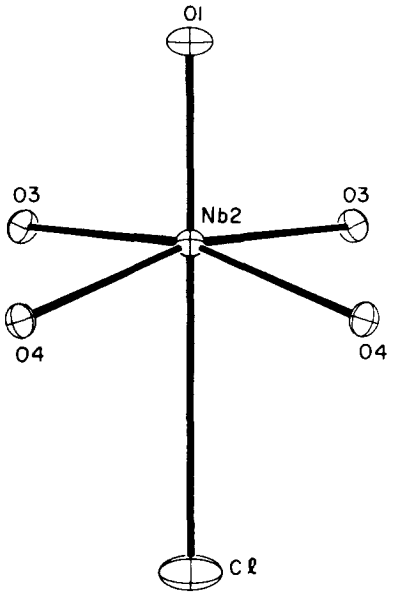

FIG. 3. Coordination of oxygen and Cl atoms in NbO_5Cl (50% thermal ellipsoids).

ters, and interatomic distances are presented in Tables II, III, and IV, respectively.

Discussion

The crystal structure of $LaNb_2O_6Cl$ is shown in Fig. 1. All atoms have site symmetry (*m*) except Nb(1), which lies on an inversion center, and O(3) and O(4), which are in general positions. The La is eightfold coordinated with six oxygens and two chlorides in an arrangement which can be described as an oxygen O(1) face-capped pentagonal bipyramid with the two chlorides occupying the apical positions (Fig. 2). The La–Cl distances are identical to those found previously in $LaWO_4Cl$ (*2*). The oxygens in the basal plane are all coordinated to three metal atoms and the La–O distances range from 2.53 to 2.67 Å. However, the face-capping O(1) is coordinated to only two metal atoms, and the La–O distance is correspondingly shortened (2.340 Å).

Nb(1) lies on a crystallographic inversion center and is octahedrally coordinated to six oxygen atoms. Here the Nb–O distances range from 1.94 to 1.99 Å.

Nb(2), which is constrained to lie on a mirror plane, is also octahedrally coordinated (Fig. 3). The Nb–O(1) distance which is *trans* to the Cl bond is again shortened by about 0.24 Å to 1.76 Å with respect to the remaining Nb–O distances. This is similar to the shortened Nb–O distance in $NbOPO_4$ (*6*) [1.78(1) Å].

The lattice is built from Nb(1) chains of corner-shared octahedra linked by the second Nb(2) octahedra sharing the common O(2),O(3) and O(3),O(4) edges, respectively, around the La pentagonal basal plane.

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