Structural Description of La$_3$NbO$_7$

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The structure of La$_3$NbO$_7$ was refined on a single crystal prepared by the flux method (R = 0.029). The unit cell is orthorhombic, with lattice parameters a = 7.747(1) Å, b = 11.149(1) Å, c = 7.611(1) Å and centrosymmetric space group *Pnma*, Z = 4. Similarly to the previous structural description proposed in the *Cmcm* space group (1), the stacking is described in terms of zigzag chains of NbO$_6$ octahedra aligned along the a axis of the crystal. The lanthanum ions lie on two different sites, for which the coordination polyhedra consist in 7 or 8 oxygen neighbors and the Nb atoms are off-centered in their octahedra. © 1995 Academic Press, Inc.

INTRODUCTION

Ln_3NbO$_7$ and Ln_3TaO$_7$ compounds were found long ago, with Ln^{III} being almost all lanthanide ions plus yttrium, and were supposed to derive from fluorite (M_4O$_8$), pyrochlore, or weberite (M_2M_2'O$_7$) types (2). The polymorphism of these compounds has been extensively investigated (1, 3–14). A defective fluorite type structure, with ordering effects, was found for the smaller Ln^{3+} ions (Dy → Lu), whereas orthorhombic superstructures are announced when the Ln^{3+} ion was larger (La → Gd), with unit-cell constants $a_{orth} \sim 2a_{fluorite}$ and $b_{orth} \sim c_{orth} \sim a_{fluorite}\sqrt{2}$.

We are more particularly interested here in La$_3$NbO$_7$, the first term of the niobate series, which can be considered as the model of Ln_3MO$_7$ compounds with the same structure (M = Sb, Mo, Ru, Ir) (7, 15–18). The compound La$_3$NbO$_7$ is also studied as a possible host matrix for a neodymium doped material. Therefore, the structure was established from X-ray diffraction intensities of a single crystal, in order to determine the possible sites and environments of Nd^{3+} in such a matrix.

STRUCTURAL INVESTIGATION

Experimental

The compound La$_3$NbO$_7$ is prepared by solid state reaction from the starting oxides, first calcined at 1000°C be-

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fore use, then mixed and pressed into pellets. The title phase is formed by heating for 2 days at 1500°C. As already reported (3), no clear phase transition was detected on La$_3$NbO$_7$, either by the unit cell constants evolution versus temperature, or by DTA. After flame fusion melting (about 1750°C), X-ray diffraction characterization confirms the unmodified La$_3$NbO$_7$ structure. The crystal growth is performed by the flux method through dissolution of La$_3$NbO$_7$ in lead fluoride at 1200°C and controlled evaporation of the solvent (4). The resulting crystals are pale yellow, transparent with flat-needle shape.

Crystal Structure Determination

Structure investigation was first performed by X-ray photographic methods. The observed diffraction spots on La$_3$NbO$_7$, as well as on La$_3$TaO$_7$ crystals prepared under the same conditions, are ruled by the conditions 0kl: $k + l = 2n$ and $hk0$: $h = 2n$, leading to the possible space groups *Pnma* or *Pn2$_1$a*.

The *Pnma* space group had been proposed previously by some authors (3–5, 19, 20), working on single crystals, whereas electron diffraction studies combined with X-ray powder diffraction refinement on La$_3$NbO$_7$ and Nd$_3$NbO$_7$ led to a base-centered lattice, with space group *Cmcm* (1). However, Rossell mentioned that weak electron diffraction spots forbidden in this group existed for Nd$_3$NbO$_7$ and that "the structure in *Cmcm* represented a reasonable approximation to the true one." In our study, quite a number of these reflections, forbidden for a C lattice, were observed, but they are generally rather weak. This could explain that a more symmetrical space group *Cmcm* has been assigned to the structure of Ln_3NbO$_7$ (Ln = La, Nd, Pr) because these reflections were not detected or were neglected (1, 13, 14, 18). All these descriptions resulted in an agreement factor poorer than in this work.

Intensity data were collected with a CAD4 Nonius diffractometer on a needle-like crystal of La$_3$NbO$_7$, with dimensions 0.02 × 0.05 × 0.2 mm. The operating conditions are reported in Table 1. Data reduction, intensity sorting and statistics, and empirical absorption corrections were all performed with the computing routine-pack-

TABLE 1
Crystallographic and Experimental Data for La₃NbO₇ Structure Determination

1. Crystal data

La₃NbO₇	$M = 621.62$
Space group	$Pnma$
Lattice constants	$a = 7.747(1)$ Å
	$b = 11.149(1)$ Å $Z = 4$
	$c = 7.611(1)$ Å
	$V = 657.3$ Å³
Calculated density	$\rho = 6.28$ g cm⁻³

2. Measurements

Room temperature	
Wavelength	$MoK\alpha = 0.71069$ Å
Absorption coef.	μ linear $= 208$ cm⁻¹
Minimum absorption correction	0.824
Maximum absorption correction	1.174
Crystal size	$0.02 \times 0.05 \times 0.2$ mm.
$F(000) = 1072$	
Scan mode	$\omega/2\theta$ scan
Scan speed:	1.8/20.1 degrees/min.
$0 < h < 15, 0 < k < 25, 0 < l < 15,$	$\theta_{max} = 40°$
Number of reflections of which	2090 measured
	1524 observed $(I > 3\sigma)$

3. Refinement

Extinction correction factor	0.6×10^{-6}
Number of refined parameters	57
R factor with 1195 $F(hkl)$ $(F_{min} > F_{max}/30)$	0.029
$R_w = [\Sigma w_i|\Delta F|^2/\Sigma w_i|F_{obs}|^2]^{1/2}$ $(w = 1)$	0.034

age CRYSTALS, adapted to a micro VAX II computer (21). A Patterson function yielded the positions of heavy atoms. The atomic coordinates deduced were then refined by full-matrix least-squares methods in the centric space group $Pnma$.

Indeed, Rogers' statistical test on the observed diffraction peaks indicated the absence of an inversion center, but on the other hand, no second harmonic generation

was detected on the crystal. The structure refinement was also performed with the acentric space group $Pn2_1a$, involving more variable parameters for more independent ions. It led to the same structural features and local environments, ruled by very similar values of interatomic distances, but gave results which were in no way better than those obtained with $Pnma$ (agreement and thermal factors and ESDs for coordinates were similar). However, all corresponding atomic parameters are available for comparison or discussion.

In addition, a recent transmission electron microscopy study was performed by means of a systematic method which involves identification of the possible space groups from microdiffraction followed by point group determination from convergent beam electron diffraction (CBED) (22). In agreement with our X-ray results, microdiffraction led to the possible space groups $Pnma$ or $Pn2_1a$, and the CBED whole pattern on [101] zone axis showed the presence of a mirror plane m corresponding to the centered space group $Pnma$ (23).

Refinement of occupancy factors confirmed the localization of Nb and La and showed full occupancy for all three cationic sites La$_{(1)}$, La$_{(2)}$, and Nb. As some ions exhibited abnormally high thermal factors, anisotropic refinement was carried out. Secondary extinction was introduced and refined. The final value of agreement factor R was 0.029. The corresponding atomic parameters are given in Table 2 and related interatomic distances in Table 3. Using these $M-O$ distances, bond strengths have been evaluated using empirical relations (24), and the corresponding estimated sum of bond strengths for each atom is also reported in Table 3.

DISCUSSION

The crystal is built from NbO₆ octahedra, connected by corners into zigzag chains aligned along the a axis

TABLE 2
Atomic Parameters of La₃NbO₇ Refined in $Pnma$ Space Group

Site	Atom	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B equiv
			(× 10⁴)					(× 10⁴)			(Å²)
8d	La1	2506(1)	4759(0)	4494(0)	26	13	17	1	1	−4	0.6
4c	La2	0016(5)	2500	7668(1)	28	12	71	0	−25	0	1.0
4c	Nb	9889(7)	2500	2516(1)	1	10	16	0	−2	0	0.3
8d	O1	9600(8)	3768(7)	4233(8)	39	29	83	−7	−24	34	1.4
4c	O2	2487(14)	2500	3186(9)	17	23	34	0	−2	0	0.8
8d	O3	2491(12)	3811(4)	7242(6)	33	18	20	8	19	4	0.7
8d	O4	9637(11)	8736(8)	9392(10)	47	19	39	3	−14	13	1.0

TABLE 3
Selected Bond Lengths (in Å) and Calculated Valences in La₃NbO₇ (Pnma)

Distances around cations		
La1–O3	2.341(4)	
La1–O3	2.343(5)	
La1–O4	2.491(7)	
La1–O1	2.502(8)	average La1–O = 2.487 Å
La1–O1	2.509(7)	
La1–O4	2.516(7)	
La1–O2	2.708(2)	
La2–O3 × 2	2.433(8)	
La2–O3 × 2	2.443(8)	average La2–O = 2.506 Å
La2–O4 × 2	2.642(8)	
La2–O1 × 2	2.989(7)	
Nb–O2	1.936(12)	
Nb–O1 × 2	1.938(7)	average Nb–O = 1.993 Å
Nb–O4 × 2	2.035(8)	
Nb–O2	2.076(12)	

Calculated valence for La1 $\Sigma\sigma = 3.1$
La2 $\Sigma\sigma = 2.7$
Nb $\Sigma\sigma = 4.8$

Distances and angles around oxygen atoms			
O1–Nb	1.938	La1–O1–Nb = 144.4°	
O1–La1	2.509	La1–O1–Nb = 105.7°	$\Sigma = 355.4°$
O1–La1	2.516	La1–O1–La1 = 105.3°	
O1–La2	2.989		
O2–Nb	1.936		
O2–Nb	2.076		
O2–La1	2.708		
O2–La1	2.708		
O3–La1	2.341		
O3–La1	2.343		
O3–La2	2.433		
O3–La2	2.443		
O4–Nb	2.035		
O4–La1	2.491		
O4–La1	2.502		
O4–La2	2.641		

Calculated valence for O1 $\Sigma\sigma = 1.8$
O2 $\Sigma\sigma = 2.0$
O3 $\Sigma\sigma = 2.3$
O4 $\Sigma\sigma = 1.8$

(needle axis). These [NbO₅]∞ chains involve Nb and O₍₁₎, O₍₂₎, O₍₄₎ atoms. The complement of the structure, [La₃O₂]∞ stacking, is arranged into two families of dense layers, intersecting apart from the [NbO₅]∞ chains and oriented along the {011} planes (Fig. 1). In these layers, the O₍₃₎ oxygen atoms form nearly regular tetrahedra La₄O with their lanthanum neighbors. These La–O₍₃₎ bonds are the shortest and the strongest La–O bonds of La₃NbO₇.

The average La–O₍₃₎ distance (2.37 Å) is practically the same as that found in A-La₂O₃ (2.38 Å) and pyrochlore-type La₂Zr₂O₇ (2.34 Å) for the same type of polyhedra (25, 26). Such OLa₄ units with strong bonding are structural features common to most lanthanum oxides and oxysalts (27). Conversely to the La–O₍₃₎ bonds, the La–O bonds with other oxygen atoms, which link the [La₃O₂]∞ layers to the [NbO₅]∞ chains, are much weaker. The looser bonding of O₍₁₎ and O₍₄₎ atoms is confirmed by the low value of the sum of M–O bond strengths around these atoms ($\Sigma s \sim 1.8$) with respect to their expected valence charge (2.0). In addition, these atoms display relatively large Debye–Waller factors.

Lanthanum ions lie on two different types of sites, with surrounding oxygen atoms arranged in 6 + 1 for La₍₁₎ and 6 + 2 for La₍₂₎. The La₍₁₎ sites offer two shorter bond lengths and could well accommodate some Nd³⁺ ions.

Apart from the orthorhombic lattice distortion and small shifts from ideal positions, the cation sublattice forms a fcc lattice, similar to the lattice of the fluorite structure. All metal atoms have 12 Nb and La neighbors at distances ranging between 3.42 and 4.3 Å. In the actual orthorhombic symmetry, the cation sublattice is quasi-A-base centered, which explains the weakness of the reflections that were missed by some authors who concluded to a nonprimitive space group.

As in the fluorite type, oxygen atoms lie in tetrahedral sites. However, these sites are highly distorted for O₍₁₎, O₍₂₎, and O₍₄₎. For the O₍₁₎ oxygen atom, one La–O₍₁₎ distance is particularly long; this atom practically lies in the plane formed by its three nearest cationic neighbors.

CONCLUSION

The structure of La₃NbO₇ is described as centric in the space group Pnma and offers two different types of possible sites for Nd³⁺ substitution. These sites have 6 + 2 or 6 + 1 neighboring oxygen ions. The shortest Ln–Ln distance (in view of optical interactions) in this host lattice is about 3.82 Å. The structure is a fluorite superstructure which may be described as the interconnection of [NbO₅]∞ chains of NbO₆ octahedra, linked by corners with a [La₃O₂]∞ network formed by OLa₄ tetrahedra. This description of the structure explains the crystal habit observed for La₃NbO₇ crystals, which are ⟨100⟩ needles with natural side faces {011}. As result of the crystal structure determination, the refined Nb position is off-centered in its octahedral environment. This is not unusual for Nb compounds (28, 29), especially in noncentrosymmetric structures showing ferroelectric behavior.
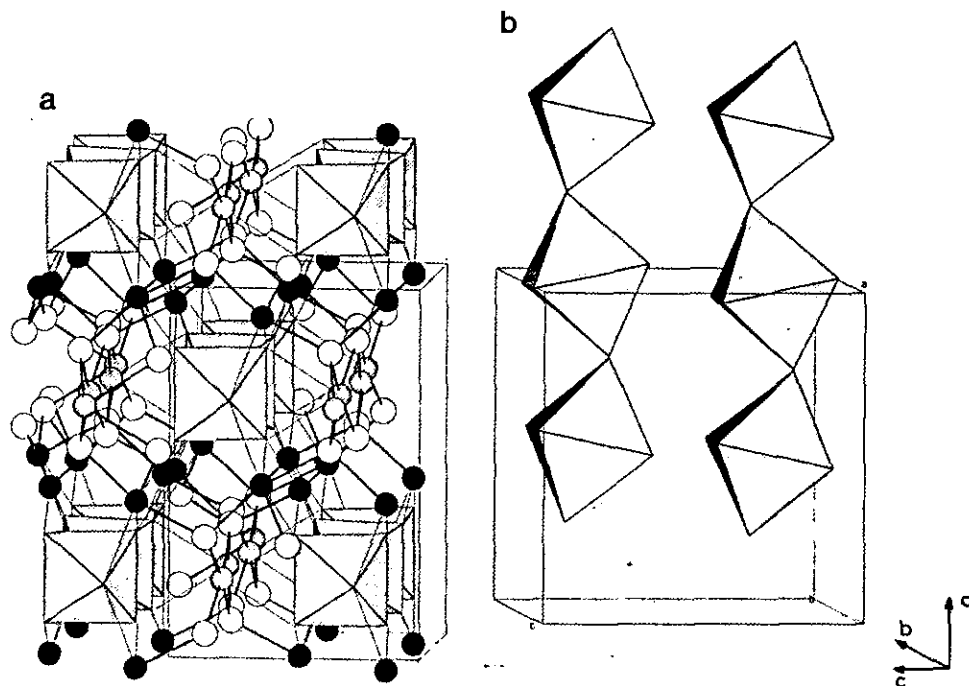
a

b

FIG. 1. (a) General view of La_3NbO_7 structure (along the a axis). Light circles are oxygen atoms. Black circles are La1 and grey circles are La2. (b) Zigzag chains of [NbO6] octahedra along the a axis. Nb–O–Nb angle 149.7° and Nb–Nb distance 3.87 Å within a chain. Drawn with MOLVIEW (J. M. Cense, ENSCP, Paris, France).

ACKNOWLEDGMENTS

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