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THE CRYSTAL STRUCTURE OF CALCIUM NIOBATE ($CaNb_2O_6$)

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ABSTRACT

Calcium niobate, $CaNb_2O_6$, crystallizes in the space group *Pbcn*. The lattice parameters are: $a=14.926\pm0.004$ Å; $b=5.752\pm0.004$ Å; and $c=5.204\pm0.004$ Å. The measured density using the displacement method was 4.70 g/cc and the density calculated assuming four formula weights per unit cell was 4.78 g/cc. The structure was determined by the heavy atom method, and the R value is 6.7 percent for 618 observed reflections. The structure consists of calcium and niobium atoms surrounded by oxygen atoms in a polyhedral arrangement. The polyhedra share corners and edges to form a chain-like network throughout the solid.

INTRODUCTION

The structure of calcium niobate, $CaNb_2O_6$, was of interest because this particular crystal is a strong source of coherent light which can be useful in holography. Ballman and co-workers (1963), as well as Yariv and Gordon (1963), reported that it has been used both as a laser and a laser host material. Hess and Trumpour (1959) determined the cell parameters and the space group of fersmite, a mineral which is 89 percent $CaNb_2O_6$. These parameters were later refined by Rowland and coworkers (1960). While the present investigation was in progress, Aleksandrov's (1960) structure determination of natural fersmite using two-dimensional data was noted in the literature.

The crystals were furnished by E. A. Weaver (Weaver and Li, 1969).

COLLECTION AND REDUCTION OF X-RAY DATA

The space group of calcium niobate was determined to be *Pbcn* (No. 60), International Tables for X-Ray Crystallography (1952). The systematic absences were: *hkl*, none; *0kl*, $k=2n+1$, *h0l*, $l=2n+1$; and *hk0*, $h+k=2n+1$ which uniquely determined the space group as being *Pbcn*. These absences were observed both on Weissenberg patterns for the *hk0*, *hk1*, *hk2* levels as well as precession patterns for the *0kl*, *1kl*, *2kl*, *h0l*, *h1l* and *h2l* levels. Lattice parameters were determined using film data measurements and least-squares procedures.

The lattice parameters were also determined on the diffractometer using CuKα, (1.54050 Å), with a 0.05 degree receiving slit and a one degree take-off angle. The following cell parameters were obtained, with the computed standard deviations from the least-squares refinement:

$$a=14.926\pm0.004 \text{ Å}$$
$$b=5.752\pm0.004 \text{ Å}$$
$$c=5.204\pm0.004 \text{ Å}$$

The cell parameters from film measurements were in excellent agreement with those determined from the diffractometer measurements.

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The density was considered to be too large to be accurately determined using the flotation method, and was, therefore, measured using the displacement method utilizing a pycnometer and carbon tetrachloride. The density was measured as 4.70 g/cc and the calculated density assuming four formula weights per unit cell was 4.78 g/cc.

The crystal of calcium niobate was a clear, colorless rectangular parallelepiped with the dimensions of 0.126 mm $\times$0.203 mm $\times$0.403 mm. The crystal was mounted with the c^* axis, which coincided with the longest dimension, parallel to the phi axis. The linear absorption coefficient was 59.946 cm^{-1}, with a maximum transmission factor of 0.485 and a minimum of 0.306. The data were collected using MoKα (0.7107 Å) radiation, balanced filters and scintillation counter on a General Electric XRD-5 diffractometer by the stationary counter-stationary crystal technique. The total intensity was collected for a ten second period using a zirconium filter and background intensity was taken by another ten second count using an yttrium filter. Intensities of several systematic extinctions were measured indicating that all intensities with a net count of four or less were unobserved.

The total number of reflections for which intensity measurements were taken was 657. Of this number, 629 reflections were considered to be observed. Intensity data were taken

TABLE 1. NIOBIUM-NIOBIUM INTERACTIONS

	Peak Height	Coordinates
Origin:	5274	
($\frac{1}{2}$, 1, $\frac{1}{2}$+2z)	2290	($\frac{1}{2}$, $\frac{1}{2}$, 3/30)
(0, 2y, $\frac{1}{2}$)	2265	(0, 12/30, $\frac{1}{2}$)
($\frac{1}{2}$–2x, $\frac{1}{2}$, 0)	3078	(10/60, $\frac{1}{2}$, 0)

The niobium coordinates were: 0.17, 0.20, 0.30.

out to a two-theta of sixty degrees. Only the observed reflections were used in the final determination of the atomic parameters. All data were taken at 26°C ($\pm$2°).

Absorption, Lorentz and polarization corrections were applied to raw intensities to convert to structure amplitudes on an arbitrary scale.

STRUCTURE SOLUTION

A Patterson map was calculated and the Harker line at $\frac{1}{2}$-2x,$\frac{1}{2}$,0 was investigated first; see International Tables of Crystallography (1959). The niobium-niobium interactions should give large peaks on the map. The origin was the largest peak; the next largest peak found on the map was on the Harker line $\frac{1}{2}$-2x,$\frac{1}{2}$,0, and gave the value for the x coordinate of niobium. The third largest peak found upon the map was the peak found at $\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$+2z, and gave the z coordinate for niobium. The peak on the Harker line, 0,2y,$\frac{1}{2}$, was the fourth largest peak and gave the y coordinate for niobium. Table 1 summarizes the niobium-niobium interactions which were found on the Patterson map.

The calcium position was not found in the Patterson map. From the density, chemical formula and space group of calcium niobate, it was conjectured that calcium was in a special position or that vacancies existed in the structure. An electron density map was calculated using the niobium position, refined by a full-matrix least-squares procedure to phase the structure factors; this map gave the coordinates of the calcium to be 0.0, 0.23, 0.75 which is the Wyckoff position "c", a special position. A full-matrix least-squares re-

TABLE 2. THE FINAL ATOMIC PARAMETERS FOR $CaNb_2O_6$

Atom	[a]x	y	z	$B(10^5)$ Å^2
Ca	0.0	0.2244 (6)	0.7500	—[b]
Nb	.1653 (1)	.3166 (2)	.2987 (2)	—[b]
O (1)	.0893 (6)	.0997 (14)	.4040 (18)	1.4988
O (2)	.1003 (6)	.4280 (14)	.0056 (18)	1.8431
O (3)	.2576 (6)	.1351 (14)	.1266 (17)	.4638

Atom	[c]β (11)	β (22)	β (33)	β (12)	β (13)	β (23)
Ca	48 (16)	235 (102)	283 (128)	0 (0)	−34 (13)	0 (0)
Nb	2 (1)	98 (22)	332 (31)	4 (2)	11 (4)	30 (5)

[a] x, y, z are in fractional coordinates of the unit cell. The standard deviation of least significant digits is given in parentheses.

[b] The atom is refined anisotropically.

[c] Anisotropic thermal parameters are in the form:

$$\exp-(\beta(11)h^2+\beta(22)k^2+\beta(33)l^2+2\beta(12)hk+2\beta(13)hl+2\beta(23)kl)$$

finement of niobium and calcium and isotropic temperature parameters was carried out and the oxygen positions were deduced from a difference density map.

The filters showed uniform response over the range in which data were taken. Counting times were constant and the total peak count minus background count were checked. The results were within experimental error and unit weights selected.

The atomic positions were refined by full-matrix least-squares calculations using unit weighting factors, and isotropic temperature parameters.

The scattering factor tables, Cromer and Waber (1965) in which all atoms were in the zero oxidation state, were used and refinement continued. After four cycles, all isotropic temperature factors were positive, but became very small. Therefore, the oxygen temperature factors were held constant at the values which were obtained from the fourth cycle of isotropic least-squares refinement. In the next least-squares refinement cycle, calcium and niobium temperature factors were converted to anisotropic values with a temperature factor of the form $\exp-(\beta(11)h^2+\beta(22)k^2+\beta(33)l^2+2\beta(12)hk+2\beta(13)hl+2\beta(23)kl)$. The Wyckoff position "$c$" in space group No. 60 has a restriction placed upon the anisotropic thermal motion of the atom. Because of the special symmetry of this position described by Levy (1956), the β_{12} and β_{23} are required to be zero for calcium. The final parameters for the atoms in calcium niobate are given in Table 2.

Eleven reflections were judged to be either grossly mismeasured or affected by extinction and were deleted from the final refinement. The discrepancy value, $R=\Sigma\big|\,|F_o|-|F_c|\,\big|/\Sigma|F_o|$, for 618 observed reflections is 0.067. One least-square cycle was calculated with both observed and unobserved reflections in the refinement to judge if any large errors were included in the unobserved reflections; the R value rose to 0.081.

A final difference Fourier series was computed and no false minimum was found.

DISCUSSION OF THE STRUCTURE

The interatomic distances between the atoms of calcium niobate are found in Table 3. The calcium atoms are found on the two-fold axes;

TABLE 3. INTERATOMIC DISTANCES FOR $CaNb_2O_6$ IN Å
(standard deviations $\times 10^3$ in parentheses)

Nb-O (1)	1.774 (9)
Nb-O (2)	1.919 (9)
Nb-O (3)''	2.077 (9)
Nb-O (3)	1.947 (9)
Nb-O (2)'	2.065 (9)
Nb-O (3)'	2.342 (8)
Nb-Ca	3.448 (1)
Ca-O (1)	2.353 (9)
Ca-O (2)	2.319 (9)
Ca-O (1)'	2.427 (8)
Ca-O (2)''	2.322 (9)

therefore, the independent interatomic distances for calcium-oxygen are reduced to four. The prime, double prime, and triple prime symbols are used in the tables to designate oxygen atoms which are symmetry relatives of the original oxygen positions in the unit cell.

The atoms in calcium niobate have little thermal motion. RMS displacements from equilibrium positions along the principal axis of thermol motion are listed in Table 4.

The magnitudes of the structure factors for the calcium niobate are found in Table 5. They include all the diffraction data taken out to 60° in two theta. F_o is the observed structure factor and F_c is the calculated structure factor.[2]

The structure of $CaNb_2O_6$ is similar to the columbite structure, $FeNb_2O_6$ reported by Sturdivant (1930). A polyhedron of oxygen atoms about each calcium or niobium atom is the main structural feature (Figure 1). Each niobium octahedron shares two edges with adjoining

TABLE 4. RMS DISPLACEMENT FROM EQUILIBRIUM POSITION ALONG PRINCIPAL AXES OF THERMAL MOTION
(The displacements are in Å.)

Atom	Axis 1	Axis 2	Axis 3
Ca	0.056	0.079	0.085
Nb	.014	.054	.069
O (1)	.044	.044	.044
O (2)	.048	.048	.048
O (3)	.024	.024	.024

[2] Table 5 listing the structure factors may be ordered as NAPS document #00708 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th Street, New York, New York 10001; remitting in advance $1.00 for microfiche or $3.00 for photo copies, payable to ASIS-NAPS.

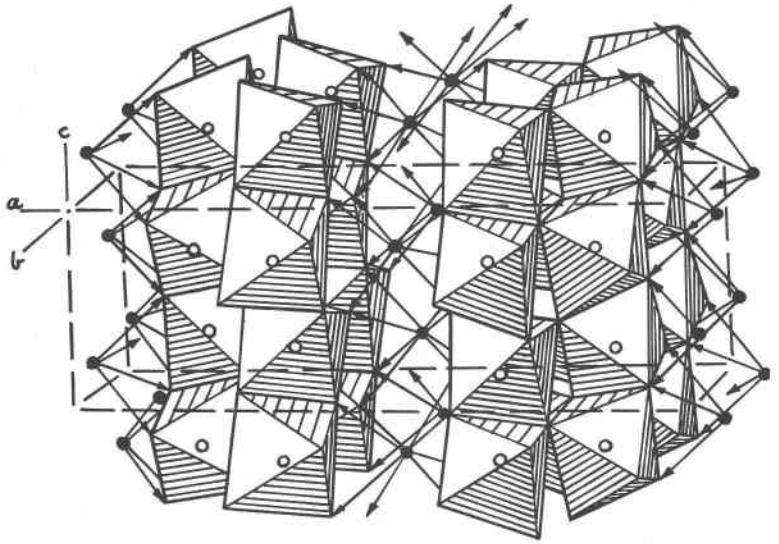

FIG. 1. An artist's conception of the octahedral arrangement of oxygen atoms surrounding calcium and niobium atoms in the unit cell of calcium niobate; black circles are calcium; open circles are niobium. There are four calcium, eight niobium and twenty four oxygen atoms per unit cell.

niobium octahedra which form chains of octahedra through the solid. The niobium octahedra are linked to each other along their shortest edges. The chains of niobium octahedra are oriented along the *c* axis. The chains of the niobium octahedra are connected to each other through the calcium atoms, which forms a distended or irregular cuboid of oxygen atoms about the calcium atom. This irregular cube-shape is very distorted. The calcium polyhedra are more distorted than the niobium octahedra. Table 6 lists the oxygen-oxygen interatomic distances and Table 7 has the bond angles found in the niobium octahedron.

Aleksandrov used natural occurring fersmite, which is 89 percent calcium niobate, as well as two-dimensional data to obtain the structure with an *R* value of 14.5. The two-dimensional structure determination was calculated using fractional valences for oxygen and fractional weights for calcium to rare earth and niobium to titanium ratios. In the present determination, the crystal was pure calcium niobate, and valence states were not found to be fractional. The better refinement was possible because more data was taken; it was three-dimensional; also, data were corrected for absorption of X radiation (linear absorption coefficient 59.946).

Shiozaki and Mitsui (1963) report niobium-oxygen bond distances of 1.904 Å to 2.168 Å in $LiNbO_3$. Abrahams and co-workers (1966) pub-

TABLE 6. INTERATOMIC DISTANCES FOR OXYGEN IN THE NIOBIUM OCTAHEDRON
(standard deviations $\times 10^3$ in Å in parentheses)

O (1)—O (2)	2.809 (12)
O (1)—O (3)	2.983 (12)
O (1)—O (1)″	2.844 (13)
O (1)—O (2)′	2.773 (12)
O (1)—O (3)′	2.905 (13)
O (2)—O (3)	2.920 (13)
O (2)—O (3)″	2.958 (12)
O (2)—O (2)′	2.731 (13)
O (2)—O (3)′	2.514 (12)
O (3)—O (3)″	2.928 (12)
O (3)—O (3)‴	2.885 (11)
O (3)—O (3)′	3.031 (12)

lished values of 1.889 Å to 2.168 Å for the niobium-oxygen bond in $LiNbO_3$. Gatehouse and Wadsley (1964) report niobium-oxygen bond distances in Nb_2O_5 varying between 1.73 Å and 2.26 Å for octahedral niobium. In calcium niobate, the niobium-oxygen interatomic distances vary between 1.774 Å and 2.342 Å.

The irregularity in the interatomic distances and variations from close packing in the structure of $CaNb_2O_6$ leads one to view this compound as a complex oxide and salt of $H_2Nb_2O_6$. The difference in interatomic distances is a reflection of the valence distribution being over the whole polyhedra in a coordinate system rather than on the atoms in an ionic system.

Pauling's (1964) crystal radii are 1.40 Å for oxygen and 0.99 Å for

TABLE 7. BOND ANGLES OF THE NIOBIUM OCTAHEDRON IN DEGREES
(standard deviations in parentheses)

O (1) —Nb—O (2)	99.0 (.4)
O (2) —Nb—O (3)	99.9 (.4)
O (1) —Nb—O (3)	102.6 (.4)
O (2)′—Nb—O (3)′	82.7 (.3)
O (2)′—Nb—O (3)″	74.7 (.3)
O (2)′—Nb—O (3)	162.7 (.3)
O (2)′—Nb—O (2)	86.5 (.4)
O (2)′—Nb—O (1)	92.2 (.4)
O (3)′—Nb—O (3)″	86.4 (.3)
O (3)′—Nb—O (3)	84.0 (.3)
O (3)′—Nb—O (2)	71.5 (.3)
O (3)′—Nb—O (1)	169.5 (.4)
O (3)″—Nb—O (2)	152.8 (.3)
O (3)″—Nb—O (1)	101.2 (.4)
O (3)″—Nb—O (3)	93.3 (.4)

TABLE 8. INTERATOMIC DISTANCES FOR OXYGEN IN THE CALCIUM POLYHEDRON
(standard deviations $\times 10^3$ in Å in parentheses)

O (1)—O (2)	2.809 (12)
O (1)—O (1)′	2.844 (13)
O (1)—O (2)′	2.773 (12)
O (1)′—O (1)″	3.069 (12)
O (1)′—O (2)″	3.086 (12)
O (1)′—O (2)‴	3.661 (13)
O (2)—O (2)′	3.107 (13)
O (2)—O (2)″	2.731 (13)
O (2)—O (2)‴	3.731 (13)

TABLE 9. BOND ANGLES IN DEGREES IN THE CALCIUM POLYHEDRON
(standard deviations in parentheses)

O (1)—Ca O (2)	103.2 (.3)
O (1)—Ca O (2)″	94.6 (.3)
O (2)—Ca O (2)″	119.4 (.3)
O (2)″–Ca O (1)′	158.6 (.3)
O (1)—Ca O (1)′	73.0 (.3)
O (2)—Ca O (1)′	81.1 (.3)

calcium, giving an oxygen-calcium distance of 2.39 Å which compares favorably with the average 2.355 Å found in this investigation. The interatomic distances of the oxygen atoms in the calcium polyhedron are given in Table 8, and the bond angles are given in Table 9.

The packing of the polyhedra in calcium niobate can be viewed in the three-dimensional packing diagrams by Johnson's ORTEP program (1965) (Figure 2). This view shows the chaining of niobium octahedra and calcium polyhedra through the solid. The polyhedra in $CaNb_2O_6$ are connected in an infinite net by the sharing of edges and corners of the chains of niobium octahedra and calcium polyhedra.

The calcium-calcium interatomic distance is 3.665 Å. The closest niobium-niobium interatomic distance is 3.351 Å and the longest inter-

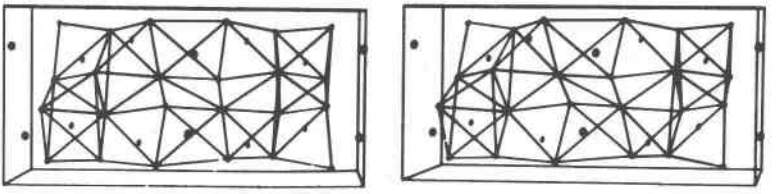

FIG. 2. Stereoscopic view of the packing of calcium niobate in the unit cell. *a* is to the right, *c* is up, and *b* is coming out of the page.

atomic niobium-niobium distance is 3.829 Å. In the niobium metal structure reported by Horn and Ziegler (1947), the second closest neighbor distance is 3.301 Å, which is reasonably close to the niobium-niobium distance of 3.351 Å. However, a metal-metal bond does not seem likely.

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