



CANADA

DEPARTMENT OF MINES AND
TECHNICAL SURVEYS, OTTAWA

MINES BRANCH
RESEARCH REPORT

R 48

PRICE 25 CENTS

THE CRYSTALLOGRAPHY OF COMPOUNDS
IN THE CALCIUM OXIDE-NIOBIUM PENTOXIDE
SYSTEM

by

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REPRINTED FROM THE PROCEEDINGS OF THE SEVENTH ANNUAL CONFERENCE ON
INDUSTRIAL APPLICATIONS OF X-RAY ANALYSIS, HELD AT DENVER, COLORADO
ON AUGUST 13, 14, AND 15, 1958.

JUNE 8, 1959

01-7991773

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by

John F. Rowland^A, Norman F. H. Bright^A and Arnout Jongejan^A

ABSTRACT

In the course of work on the $\text{CaO-Nb}_2\text{O}_5\text{-SiO}_2$ system, a series of compositions on the $\text{CaO-Nb}_2\text{O}_5$ binary join has been studied. There are indications of the existence of three calcium niobates. These compounds have been characterized by X-ray powder diffraction and optical data. Single crystal studies have given information concerning the crystallography of these materials.

INTRODUCTION

The current interest in niobium (columbium) has given rise to considerable activity in the study of the geochemistry of niobium-bearing deposits. One mineral that has recently been discovered in Canada, and whose crystallography has been studied, is niocalite (1, 2). This mineral is predominantly a calcium niobium

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(1, 2) For references see end of paper.

silicate with fairly extensive substitution by numerous other elements, and its discovery prompted a phase study of the simplified ternary system on which it is based, namely the system $\text{CaO-Nb}_2\text{O}_5\text{-SiO}_2$. This phase equilibrium study has been made in the laboratories of the Mines Branch, Ottawa, and the complete results of the investigation will be published elsewhere shortly. The present paper reports results obtained in the investigation of the calcium oxide-niobium pentoxide binary join of the ternary system.

The existence of three calcium niobates was briefly reported many years ago by Holmquist (3, 4), Joly (5, 6), and Larsson (7). These compounds, and their properties, as reported at the time of discovery are:

- 1) $\text{CaO.Nb}_2\text{O}_5$ or $\text{Ca}(\text{NbO}_3)_2$ - tabular crystals having a specific gravity variously given as 4.12 and 4.484
- 2) $2\text{CaO.Nb}_2\text{O}_5$ or $\text{Ca}_2\text{Nb}_2\text{O}_7$ - colourless prismatic crystals, rhombic needles, or plates having a specific gravity of 4.484
- 3) $3\text{CaO.Nb}_2\text{O}_5$ or $\text{Ca}_3(\text{NbO}_4)_2$ - no details given.

These materials were made by reaction of either niobium pentoxide or a sodium niobate with calcium chloride, carbonate, or sulphate, with subsequent acid leaching of the product.

Two occurrences of calcium niobates as natural minerals have been reported: firstly, as a hydrated niobate, $\text{CaO.Nb}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$, known as ellsworthite (8); secondly, as the mono-niobate, $\text{CaO.Nb}_2\text{O}_5$, with extensive substitution, known as fersmite (9). The former is not relevant to the present study, but the latter is similar to a compound

synthesized in these investigations.

The fragmentary information on this binary system made it desirable to verify the existence of the reported calcium niobates, and to study their crystallography and other properties, in order to assist in compiling the ternary phase diagram of the $\text{CaO-Nb}_2\text{O}_5\text{-SiO}_2$ system.

EXPERIMENTAL TECHNIQUES AND RESULTS

The investigation involved chemical preparative work in order to obtain the compounds, thermal work to determine their melting points, and X-ray diffraction and optical studies to describe the crystallography. These techniques are described individually and the results obtained by each are discussed. The abbreviations CN, C_2N , and C_3N are used to refer to the three compounds $\text{CaO.Nb}_2\text{O}_5$, $2\text{CaO.Nb}_2\text{O}_5$, and $3\text{CaO.Nb}_2\text{O}_5$, respectively.

Preparation of Calcium Niobates

The materials used for the preparation of the calcium niobates were:

- a) Calcium carbonate - Baker C.P. grade reagent
- b) Niobium pentoxide - High purity material from Fansteel Metallurgical Corporation, North Chicago.

These powders were blended in appropriate proportions by prolonged grinding in an agate mortar, sintered overnight in platinum crucibles at 1000°C to decompose the carbonate, and then heated in a natural gas/oxygen-fired furnace to 1700°C for one hour, care being taken to

maintain an oxidizing condition inside the furnace. The materials having compositions corresponding to the compounds CN , C_2N , and C_3N all appeared to be molten under these conditions. The melts were quenched to room temperature by water immersion. There was no tendency towards glass formation with this treatment, and all three products were well crystallized, the development being greatest for CN , and least for C_3N . Suitable portions of the products were then examined by X-ray diffraction and optical methods.

The stoichiometric compositions of the mixtures and the interpretations of the X-ray diffraction patterns of the products are summarized below:

<u>Composition</u>	<u>Phases present</u>
$C_{0.5}N$	$N + CN$
$C_{1.0}N$	CN only
$C_{1.5}N$	$CN + C_2N$
$C_{2.0}N$	C_2N only
$C_{2.5}N$	$C_2N + C_3N$
$C_{3.0}N$	C_3N (+ trace C_2N + possible trace C)
$C_{4.0}N$	$C_3N + C$

The existence of any further niobates other than CN ($CaO.Nb_2O_5$), C_2N ($2CaO.Nb_2O_5$), and C_3N ($3CaO.Nb_2O_5$) is thus very unlikely.

Thermal Work on Niobates

Cone-fusion melting points were determined on the three single-phased quenched products, prepared as described above, and also on pure niobium pentoxide. The temperatures at which the cones started to deform and at which they had completely slumped were observed, giving respectively estimates of the solidus and liquidus temperatures. The experiments were conducted in an air atmosphere in a platinum/rhodium-wound tube furnace.

The following results were obtained:

1) Niobium pentoxide (Nb_2O_5)

Started to melt at 1470°C , completely molten at 1480°C .
X-ray diffraction showed the product to consist of Nb_2O_5 only.
The original creamish-white colour was retained.

2) CN ($\text{CaO} \cdot \text{Nb}_2\text{O}_5$)

Melted very sharply and completely at 1560°C .
X-ray diffraction indicated that the product was unchanged from the original material.

3) C_2N ($2\text{CaO} \cdot \text{Nb}_2\text{O}_5$)

Started to melt at 1565°C , completely molten at 1575°C .
The product again appeared to be unchanged from the original material.

4) C_3N ($3\text{CaO} \cdot \text{Nb}_2\text{O}_5$)

Indication of start of melting at 1570°C , approximately;
melted fairly sharply but only partially at 1615°C ;
portion of cone left unmelted at 1700°C , the maximum temperature to which the experiment was taken.

The product, when examined by X-ray diffraction, appeared to correspond to a mixture of the original material, with an appreciable amount of C_2N ; the presence of free CaO was also possible, although lines corresponding to CaO would be, to a large extent, masked by the more complex niobate patterns.

This behaviour is consistent with incongruent melting.

The results of the cone-fusion work can be summarized as follows:

<u>Compound</u>	<u>Melting Point</u>	<u>Nature of Melting</u>
Nb_2O_5	1480°C	Congruent
CN	1560°C	Congruent
C_2N	1575°C	Congruent
C_3N	1615°C	Incongruent

In view of the evidence of incongruent melting obtained for C_3N , the material chosen for the crystallographic studies was a sample prepared by solid state sintering at a temperature below 1615°C, where the C_2N impurity was considerably less, and the degree of crystallinity of C_3N was greater.

X-Ray Diffraction and Optical Studies

1. General Remarks

The powder diffraction patterns of the three compounds occurring in the CaO- Nb_2O_5 binary system were obtained with 114.6 mm diameter Debye-Scherrer camera and filtered copper and cobalt radiations. Single crystals of the compounds CN and C_2N were available for Weissenberg and precession camera studies, and photographs were obtained using both molybdenum and copper radiations.

The powder diffraction patterns of these two compounds were indexed from the crystallographic data determined from the single crystal films. No single crystals of the compound C_3N were available, but, nevertheless, a logical interpretation of the powder diffraction pattern was found to be possible.

The unfavourable morphological characteristics, in combination with the high refractive indices, of the two compounds for which single crystals were available, prevented the direct determination of all the optical constants with the available instruments.

For the determination of the refractive indices the techniques described by Merwin and Larsen (10) were followed to a considerable extent. Cooled amorphous mixtures containing appropriate proportions of sulphur and selenium were prepared, and used as embedding media of known refractive indices. The refractive index of each mixture could not be checked by measurement as no suitable prism was available, but was obtained from the data given by Merwin and Larsen. Several mixtures, having the same sulphur - selenium proportions, were used for the limiting determinations, however, and no differences in results were found. Also, there was very little difference between the wavelengths for which the refractive index of the embedding medium and that of the crystal matched exactly. It was concluded, therefore, that the sulphur - selenium proportion did not change to any appreciable extent during the preparation of the mixtures.

The optical angle was determined directly by use of the Fedorov universal stage, and was confirmed by measurement of the interference figure proper. In the latter case, the equation $\sin E = d/K$ was used, where d = half the distance between the two isogyres, and K = a constant for the particular lens combination used. The value of K was determined by measurement of the optical constants of a mica flake.

Once the axial angle and two of the refractive indices had been measured, the third refractive index was calculated according to the equation

$$\tan^2 V_{\gamma} = \frac{\frac{1}{\alpha^2} - \frac{1}{\beta^2}}{\frac{1}{\beta^2} - \frac{1}{\gamma^2}}$$

It should be kept in mind that no ordinary compensators could be used because of the high birefringence of the materials under investigation.

2. CN (CaO.Nb₂O₅) Detailed Results

Colourless to faintly yellow prismatic crystals of CN were obtained. The interpretation of the single crystal photographs gave the following crystallographic data:

Crystal System: Orthorhombic

Extinction Rules: $(hk\ell)$ all present
 $(0k\ell)$ only with $\ell = 2n$
 $(h0\ell)$ only with $h = 2n$
 $(hk0)$ only with $h + k = 2n$

Space Group: $Pcan - D_{2h}^{14}$ (uniquely determined)

Cell Dimensions: $a = 5.73$, $b = 14.94$, $c = 5.22$ Å

Axial Ratio: $a : b : c = 0.384 : 1 : 0.349$

Cell Volume: 446.86 Å³

Optical goniometer observations of several crystals showed that they were elongated $[001]$ and flattened (010) . The only forms present were (010) and (110) , the prism ends being generally rough. Goniometric measurements showed $(010) \wedge (110) = 69^\circ 00'$, with $a : b = 0.384 : 1$, which is in accord with the X-ray data.

The measured specific gravity, using a pycnometer and carbon tetrachloride, is 4.72. The unit cell contains 4 molecules of $\text{CaO} \cdot \text{Nb}_2\text{O}_5$, and has a molecular weight of 1287.6. The calculated specific gravity is 4.78.

It was difficult to orient the prismatic crystals of CN in the viscous media in such a way that the refractive index in the direction perpendicular to (010) could be measured. In addition, the optical data determinations were complicated by the tendency of the CN crystals embedded in the viscous media to shatter with the slightest pressure. Unequivocal measurements were difficult to obtain because of the lemniscate patterns caused by even minor unevenness in the

surface of the crystals.

The optical properties of CN are as follows:

Biaxial positive

+ $2V = 62^\circ$ (universal stage)
 63° (interference figure)

$n_X = \alpha = 2.07$ (calculated from β , γ , and $2V$ using more precise values than those given here)

$n_Y = \beta = 2.10$ (checked with high index oils)

$n_Z = \gamma = 2.19$

Birefringence $\gamma = \alpha = 0.12$

Optical orientation: $X = b$, $Y = a$, $Z = c$

The morphological and optical properties of CN are in accord with those of the mineral fersmite, which is essentially $\text{CaO} \cdot \text{Nb}_2\text{O}_5$, with minor amounts of Ce, Na, Ti, Fe, Al, OH, and F. The data of Bohnstedt-Kupletskaya and Burova (9) include the following:

Orthorhombic, imperfect crystals

Main forms: (010), (110), and (111); (130) common; (131) and (021) rare

Axial ratio: $a : b : c = 0.377 : 1 : 0.356$

Measured specific gravity 4.69

Biaxial (probably positive), $2V$ large

Refractive indices: about 2

Birefringence: medium (not in accord with CN)

No fersmite was available to the present authors in order to compare this mineral with CN by X-ray diffraction methods.

The powder diffraction pattern of CN was indexed readily from the single crystal data. The spacings of the observed lines down to 1.5 Å, with visually estimated intensities are given in Table 1.

TABLE 1

CN (CaO.Nb₂O₅): X-RAY POWDER DIFFRACTION DATA

Orthorhombic, P_{ca}n - D_{2h}¹⁴; a = 5.73, b = 14.94, c = 5.22 Å

I	d(meas) (Å)	d(calc) (Å)	(hkl)	I	d(meas) (Å)	d(calc) (Å)	(hkl)
4	7.47	7.47	020	1	2.004	2.004	142
						2.000	170
2	5.34	5.35	110	2	1.962	1.966	052
		3.76	130	3	1.927	1.930	202
6	3.75	3.74	111			1.923	251
		3.73	040	$\frac{1}{2}$	1.916	1.914	212
2	3.428	3.429	121	4	1.879	1.880	260
10	3.049	3.051	131	5	1.799	1.802	062
3	2.863	2.865	200			1.800	232
1	2.681	2.684	141	3	1.784	1.784	330
		2.675	220			1.781	311
2	2.606	2.612	002	5	1.768	1.769	261
1	2.564	2.573	012	2	1.688	1.688	331
3	2.510	2.512	201			1.681	181
3	2.489	2.490	060	1	1.653	1.656	113
$\frac{1}{2}$	2.368	2.363	151			1.653	072
						1.626	271
1	2.306	2.313	032	3	1.622	1.626	123
						1.621	252
2	2.242	2.243	231			1.618	341
1	2.139	2.145	132	2	1.576	1.580	133
		2.140	042	7	1.537	1.538	351
2	2.090	2.093	161			1.534	312
		2.085	241				

3. C₂N (2CaO.Nb₂O₅) Detailed Results

The crystals of C₂N consisted of colourless to light yellow plates, generally in masses with numerous orientations. Except for a few poorly-formed, striated faces, which were not identified, no forms were observed in addition to the apparently well-formed faces parallel to the pronounced platy cleavage.

Initial difficulties encountered in interpreting the single crystal X-ray films were resolved by the discovery that twinning occurs in the thicker plates. The striations observed parallel to the cleavage plane may represent multiple twinning; this would conform with the twinning law established.

The interpretation of the single crystal photographs of an extremely thin platelet (where no twinning was apparent) gave the following crystallographic data:

Crystal System: Monoclinic

Extinction Rules: (hkℓ) all present
(h0ℓ) all present
(0k0) only with k = 2n

Possible Space Groups: P2₁/m — C_{2h}² or P2₁ — C₂²

Cell Dimensions: a = 13.36, b = 5.50, c = 7.70 Å, β = 98°25'

Axial Ratio: a : b : c = 2.431 : 1 : 1.400

Cell Volume: 559.4 Å³

The cleavage plane was identified as (100), and the twinning relationship present can be explained by the following twin law: twin plane = composition plane = (100). The twinned crystals

exhibit a pseudo-orthorhombic symmetry, and the X-ray diffraction photographs can be indexed on the following pseudo-cell:

$$a_o = 4a \sin \beta = 52.9, b_o = b = 5.50, c_o = c = 7.70 \text{ \AA},$$

where a , b , c , and β are the elements of the true monoclinic cell.

The measured specific gravity is 4.39, the monoclinic unit cell contains 4 molecules of $2\text{CaO} \cdot \text{Nb}_2\text{O}_5$, and the molecular weight is 1511.9. The calculated specific gravity is 4.49.

Because of the micaceous nature of the crystals of the compound C_2N , the refractive index in the direction perpendicular to (100) could not be determined conveniently. This index was therefore calculated from the other data. The optical angle was readily measured on the Fedorov universal stage, and the value obtained was checked using the interference figure. Although the orientation could not actually be related to the structure by measurement, the apparent orientation is given below.

The optical properties of C_2N are as follows:

Biaxial negative

$$\begin{aligned} -2V &= 29^\circ \quad (\text{universal stage}) \\ &30^\circ \quad (\text{interference figure}) \end{aligned}$$

$$n_X = \alpha = 1.97 \quad (\text{calculated from } \beta, \gamma, \text{ and } 2V \text{ using more precise values than those given here})$$

$$n_Y = \beta = 2.16$$

$$n_Z = \gamma = 2.17$$

$$\text{Birefringence } \gamma - \alpha = 0.20$$

$$\text{Optical orientation: } X \wedge a = 8^\circ 25', Y = b, Z = c \quad (X = a_o)$$

The powder diffraction pattern of C_2N was indexed from the single crystal data, and the spacings of the observed lines down to 1.5 Å, with visually estimated intensities are given in Table 2.

TABLE 2

 C_2N ($2CaO \cdot Nb_2O_5$): X-RAY POWDER DIFFRACTION DATAMonoclinic, $P2_1 / m - C_{2h}^2$ or $P2_1 - C_2^2$; $a = 13.36$, $b = 5.50$, $c = 7.70$ Å, $\beta = 98^\circ 25'$

I	d(meas) (Å)	d(calc) (Å)	(hkl)	I	d(meas) (Å)	d(calc) (Å)	(hkl)
6	13.08	13.22	100	8	1.918	1.926	422
2	4.98	5.08	110			1.924	$\bar{1}04, 322$
1	4.39	4.41	300			1.910	512
8	4.21	4.23	210	6	1.900	1.906	520, $\bar{2}04$
4	3.79	3.81	$\bar{1}02, 002$			1.903	004
1	3.512	3.530	$\bar{2}02$			1.800	$\bar{7}02, \bar{2}14$
		3.523	102	1	1.790	1.799	014
4	3.422	3.439	310			1.796	602
9	3.291	3.305	400	8	1.778	1.781	$\bar{5}22$
		3.130	$\bar{1}12, 012$			1.779	422
2	3.117	3.115	$\bar{3}02$	2	1.746	1.752	$\bar{3}14$
		3.108	202			1.750	114
7	2.954	2.970	$\bar{2}12$	3	1.706	1.711	$\bar{7}12$
		2.967	112			1.708	612
5	2.824	2.833	410	1	1.688	1.692	330
3	2.740	2.749	020	1	1.675	1.680	$\bar{4}14$
		2.710	$\bar{3}12$			1.678	214
10	2.698	2.706	212	2	1.658	1.665	$\bar{5}04$
		2.699	$\bar{4}02$			1.661	304
		2.692	302, 120	2	1.619	1.626	$\bar{2}32, 132$
3	2.636	2.644	500			1.604	$\bar{8}02$
1	2.540	2.538	220	1	1.600	1.603	430
2	2.377	2.383	510			1.601	702
3	2.327	2.338	$\bar{5}02$	1	1.588	1.593	$\bar{5}14$
		2.332	402, 320			1.590	314
1	2.220	2.229	$\bar{1}22, 022$	6	1.572	1.579	$\bar{3}32, 232$
5	2.107	2.114	420			1.576	$\bar{1}24$
1	2.055	2.061	$\bar{3}22$	1	1.552	1.554	404
		2.059	222	2	1.534	1.537	712
						1.534	$\bar{3}24, 124$
						1.506	530, $\bar{7}22$
				1	1.502	1.504	622
						1.499	$\bar{6}14$

It should be noted that only diffractions having $\ell = 2n$ are needed to index the powder diffraction pattern. This is in accord with the fact that in the single crystal photographs these diffractions are much more intense than those having $\ell \neq 2n$.

4. $C_3N(3CaO.Nb_2O_5)$ Detailed Results

Attempts to synthesize C_3N resulted in a fine-grained material with a distinctive powder diffraction pattern. The specimens examined were not completely pure, as trace amounts of C_2N were present in all cases. The presence of CaO, which would be necessary to satisfy the stoichiometric $3CaO:Nb_2O_5$ ratio, could not be confirmed due to the masking of its diffractions by the dominant pattern.

The strongest diffractions can be readily interpreted as representing a face-centred cubic phase, with the unit cell dimension, $a = 7.978 \text{ \AA}$. The majority of the remaining diffractions can be indexed on a primitive cubic cell with $a = 11.967 \text{ \AA}$ ($= 7.978 \times 3/2$), and the remainder, except for those due to trace amounts of C_2N and several weak lines which were unidentified, can be indexed on a face-centred cubic cell with $a = 23.934 \text{ \AA}$ ($= 7.978 \times 3$).

It is possible that C_3N crystallizes with a perovskite-type structure, with no apparent distortion of the basic cubic cell. It is hoped that further experiments will result in material suitable for single crystal X-ray diffraction studies which will determine the crystallography of this compound more completely.

The measured specific gravity is 4.23 and, if one considers the face-centred cube with unit cell dimension $a = 7.978 \text{ \AA}$, the cell volume is 507.8 \AA^3 . The unit cell contains 3 molecules of $3\text{CaO} \cdot \text{Nb}_2\text{O}_5$, the molecular weight is 1302.2, and the calculated specific gravity is 4.28.

The powder diffraction pattern obtained using filtered cobalt radiation consisted of numerous well-defined lines throughout. The spacings of the observed lines down to 1.5 \AA , the visually estimated intensities, and the interpretation based on the various above-mentioned cell dimensions are given in Table 3. All unidentified lines occur in this region of the film.

TABLE 3

 C_2N ($3\text{CaO} \cdot \text{Nb}_2\text{O}_5$): X-RAY POWDER DIFFRACTION DATACubic, Various Cell Dimensions as Indicated

I	d(meas) (\AA)	d(calc) (\AA)	$h^2 + k^2 + l^2$ values			C_2N (d)		CaO (e)	
			(a)	(b)	(c)	d(\AA)	I	d(\AA)	I
4	13.92	13.82			3				
$\frac{1}{2}$	13.12					13.08	6		
1	9.22								
2	8.48	8.46		2	8				
1	7.23	7.22			11				
1	6.89	6.91		3	12				
						4.98	2		
1	4.87	4.89		6	24				
4	4.60	4.61	3		27				
2	4.22	4.23		8	32	4.21	8		
8	3.99	3.99	4	9	36				
1	3.80	3.78		10	40	3.79	4		
$\frac{1}{2}$	3.60	3.61		11	44				
1	3.440	3.455		12	48	3.422	4		
1	3.352	3.351			51				
2	3.304	3.319		13	52	3.291	9		

(continued)

TABLE 3 (cont' d)

I	d(meas) (A)	d(calc) (A)	$h^2 + k^2 + l^2$ values			C_2N (d)		CaO (e)	
			(a)	(b)	(c)	d(A)	I	d(A)	I
1	3.196	3.198		14	56				
1	3.122	3.116			59	3.117	2		
1	2.963					2.954	7		
2	2.863							Unidentified	
10	2.820	2.821	8	18	72	2.824	5		
2	2.786	2.764			75			2.778	3
						2.740	3		
2	2.707					2.698	10		
1	2.641					2.636	3		
1	2.611	2.611		21	84				
2	2.508	2.509			91				
1	2.418							Unidentified	
2	2.404	2.405	11		99			2.405	10
1	2.380	2.393		25	100	2.377	2		
						2.327	3		
1	2.298	2.303	12	27	108				
2	2.227	2.222		29	116				
1	2.154	2.158			123				
1	2.110			32	128	2.107	5		
1	2.088	2.083		33	132				
1	2.024	2.023		35	140				
7	1.994	1.995	16	36	144				
1	1.936	1.941		38	152				
1	1.919	1.922			155	1.918	8		
1	1.905					1.900	6		
1	1.868	1.869		41	164				
2	1.829	1.830	19		171				
1	1.802	1.804		44	176				
5	1.782	1.784	20	45	180	1.778	8		
1	1.761	1.764		46	184				
						1.746	2		
1	1.709	1.710		49	196	1.706	3	1.701	4
						1.658	2		
3	1.642	1.644		53	212				
6	1.627	1.629	24	54	216				
2	1.618	1.617			219	1.619	2		
2	1.609							Unidentified	
1	1.575	1.571		58	232	1.572	6		
1	1.554	1.558		59	236	1.552	1		
2	1.535	(1.535	27		243	1.534	2		
		(1.532		61	244				

Notes: (a) Face-centred cubic unit cell dimension $a = 7.978 \text{ \AA}$

(b) Primitive cubic unit cell dimension $a = 11.967 \text{ \AA}$

(c) Face-centred cubic unit cell dimension $a = 23.934 \text{ \AA}$

(d) Weakest diffractions omitted; see Table 2 for complete C_2N powder diffraction pattern

(e) Standard data from A.S.T.M. Card Index.

CONCLUSIONS

The existence of three compounds only in the $\text{CaO-Nb}_2\text{O}_5$ binary system has been established. The crystallographic and optical data for two of these, CN ($\text{CaO.Nb}_2\text{O}_5$) and C_2N ($2\text{CaO.Nb}_2\text{O}_5$), have been determined, and the former has been shown to correspond to the naturally occurring mineral fersmite. The third compound, C_3N ($3\text{CaO.Nb}_2\text{O}_5$), has been identified, but further work, including single-crystal X-ray diffraction studies, is necessary to characterize it completely.

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JFR:NFBH:AJ:CL

THE QUEEN'S PRINTER AND CONTROLLER OF STATIONERY
OTTAWA, 1959