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Compounds with Perovskite-Type Slabs.
III. The Structure of a Monoclinic Modification of $Ca_2Nb_2O_7$

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Abstract

The crystal structure of a monoclinic modification of $Ca_2Nb_2O_7$, synthesized by a floating-zone method on an image furnace, has been determined. The cell dimensions are $a = 7{\cdot}697\,(2)$, $b = 13{\cdot}385\,(6)$, $c = 5{\cdot}502\,(1)$ Å and $\gamma = 98{\cdot}34\,(6)°$, and the space group is $P2_1$. The final R value is 0·039 for 2329 observed reflexions. The structure is based on a stack of slabs with a perovskite-type structure as in orthorhombic $Ca_2Nb_2O_7$. The difference between the two modifications exists in the stacking modes of the slabs. The orthorhombic structure is obtained by stacking unit cells of the monoclinic structure along the b axis followed by the operation of an n glide parallel to (010). The relation is somewhat similar to that between the ortho- and clinopyroxenes. Both modifications of $Ca_2Nb_2O_7$ are thought to originate from an imaginary prototype with the symmetry *Cmcm*.

Introduction

Two modifications are known for $Ca_2Nb_2O_7$ at room temperature, one being orthorhombic and the other monoclinic. The approximate structure of the monoclinic modification was described by Brandon & Megaw (1970), although no atomic parameters were given. They reported that the crystal is constructed from slabs of a perovskite-type structure with a thickness corresponding to twice the face diagonal of the perovskite cube. Scheunemann & Müller-Buschbaum (1974) determined the structure of the orthorhombic modification, revealing that it consists of the same perovskite-type slabs as those in the monoclinic crystals. The two modifications of $Ca_2Nb_2O_7$ have equal a and c lengths within experimental error. The b length of the orthorhombic form corresponds to $2b \sin \gamma$ of the monoclinic one. Gasperin (1975) determined the structure of monoclinic $La_2Ti_2O_7$, showing that the crystal is isostructural with monoclinic $Ca_2Nb_2O_7$. The present authors reported the structures of $Sr_2Nb_2O_7$ (Ishizawa, Marumo, Kawamura & Kimura, 1975) and $Sr_2Ta_2O_7$ (Ishizawa, Marumo, Kawamura & Kimura, 1976), which also belong to this structural family. Both crystals are orthorhombic with the same b and c periods as in orthorhombic $Ca_2Nb_2O_7$, but the a length is halved compared to $Ca_2Nb_2O_7$. The polymorphs of $A_2B_2O_7$ compounds with perovskite-type slabs observed at room temperature are supposed to originate from an imaginary prototype. The structure determination of monoclinic $Ca_2Nb_2O_7$ was thus undertaken, in the first place to elucidate the structural relation between monoclinic $Ca_2Nb_2O_7$ and the orthorhombic form, and secondly to compare the structure to other members of this family.

Experimental

A crystal of $Ca_2Nb_2O_7$, synthesized by the floating-zone method on an image furnace from a mixture of CaO and Nb_2O_5 (Nanamatsu & Kimura, 1974), was used for the X-ray investigation. It is colorless and transparent, having perfect cleavages parallel to (010). The space group was determined to be $P2_1$ from the Laue symmetry, the extinction rule, $00l$ with l odd, and the ferroelectric properties shown by the crystal. The cell dimensions were determined with the least-squares procedure from ten 2θ values in the range between 27 and 54° measured on an automated four-circle diffractometer with Mo $K\alpha$ radiation. The crystal data are given in Table 1.

Intensity data were collected on the four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation, utilizing a specimen with dimensions of about $0{\cdot}12 \times 0{\cdot}03 \times 0{\cdot}18$ mm. The ω–2θ scan technique was employed with a scanning speed of 1° $\min^{-1}$ in ω. Within the range $2\theta < 80°$, 2329 independent reflexion data, which satisfied the con-

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dition $|F_o| > 3\sigma(|F_o|)$, were obtained and used for the structure determination after correction for Lorentz, polarization and absorption factors. The absorption correction was carried out with the program *ACACA* (Wuensch & Prewitt, 1965) by taking into account the crystal shape. Starting from the atomic parameters of monoclinic $La_2Ti_2O_7$ (Gasperin, 1975), the structure was refined by the least-squares program *LINUS* (Coppens & Hamilton, 1970) with anisotropic temperature factors for metal atoms and isotropic ones for O atoms. After correction for secondary-extinction effects in the isotropic mode, the *R* value was reduced to 0·039 for all observed reflexions. Unit weights were given to all the reflexions in the least-squares calculations. The atomic scattering factors and dispersion-correction factors were taken from *International Tables for X-ray Crystallography* (1974). The final positional and thermal parameters are given in Table 2.* Selected bond lengths are listed in Table 3.

Table 1. *Crystal data for* $Ca_2Nb_2O_7$

Crystal system	Monoclinic
Space group	$P2_1$
Cell dimensions	$a =$ 7·697 (2) Å
	$b =$ 13·385 (6)
	$c =$ 5·502 (1)
	$\gamma =$ 98·34 (6)°
Cell volume	560·8 (3) Å^3
Z	4

Table 2. *Positional and thermal parameters for* $Ca_2Nb_2O_7$, *with estimated standard deviations in parentheses*

	x	y	z	B (Å^2)
Ca(1)	0·2285 (2)	0·9106 (1)	0·7599 (6)	0·70 (3)*
Ca(2)	0·1405 (2)	0·5681 (1)	0·3432 (6)	0·65 (3)*
Ca(3)	0·7184 (2)	0·8798 (1)	0·75	0·62 (3)*
Ca(4)	0·6428 (2)	0·6026 (1)	0·2767 (7)	0·98 (3)*
Nb(1)	0·47430 (8)	0·88302 (5)	0·2602 (5)	0·37 (2)*
Nb(2)	0·41239 (8)	0·67439 (5)	0·7858 (5)	0·42 (2)*
Nb(3)	0·96768 (8)	0·88464 (5)	0·2612 (5)	0·38 (2)*
Nb(4)	0·92168 (8)	0·67701 (5)	0·7814 (5)	0·42 (2)*
O(1)	0·5364 (9)	0·9800 (5)	0·534 (1)	0·68 (9)
O(2)	0·5015 (9)	0·7725 (5)	0·454 (1)	0·71 (9)
O(3)	0·4111 (9)	0·5625 (5)	0·583 (1)	0·72 (9)
O(4)	0·2237 (9)	0·8917 (5)	0·325 (1)	0·73 (9)
O(5)	0·1734 (9)	0·6973 (5)	0·683 (1)	0·68 (9)
O(6)	0·4294 (9)	0·8214 (5)	0·945 (1)	0·52 (8)
O(7)	0·3684 (10)	0·6148 (6)	0·076 (2)	0·92 (9)
O(8)	0·9528 (9)	0·9803 (5)	0·536 (1)	0·70 (9)
O(9)	0·8845 (9)	0·7753 (5)	0·457 (2)	0·74 (9)
O(10)	0·8674 (9)	0·5730 (5)	0·564 (1)	0·54 (8)
O(11)	0·7283 (9)	0·9138 (5)	0·165 (1)	0·59 (8)
O(12)	0·6737 (9)	0·6982 (5)	0·847 (2)	0·71 (9)
O(13)	0·9817 (9)	0·8199 (5)	0·948 (1)	0·58 (9)
O(14)	0·9279 (9)	0·5972 (5)	0·055 (1)	0·71 (9)

* Calculated from anisotropic thermal parameters according to the expression: $B = 4(a^2B_{11} + b^2B_{22} + c^2B_{33} + abB_{12}\cos\gamma)/3$.

Table 3. *Selected interatomic distances* (Å)

Nb(1)—O(2)	1·859 (8)	Nb(3)—O(9)	1·855 (8)
Nb(1)—O(6^{v})	1·929 (8)	Nb(3)—O(13^{v})	1·938 (8)
Nb(1)—O(4)	1·981 (7)	Nb(3)—O(4^{vii})	1·990 (7)
Nb(1)—O(1)	1·999 (8)	Nb(3)—O(8)	1·994 (8)
Nb(1)—O(11)	2·008 (7)	Nb(3)—O(11)	2·009 (7)
Nb(1)—O(1^{viii})	2·229 (8)	Nb(3)—O(8^{ix})	2·205 (7)
Nb(2)—O(7^{iii})	1·794 (9)	Nb(4)—O(10)	1·838 (7)
Nb(2)—O(3)	1·866 (8)	Nb(4)—O(14^{iii})	1·852 (8)
Nb(2)—O(5)	1·990 (7)	Nb(4)—O(5^{vii})	1·991 (7)
Nb(2)—O(12)	2·018 (7)	Nb(4)—O(12)	2·002 (7)
Nb(2)—O(6)	2·140 (7)	Nb(4)—O(13)	2·111 (7)
Nb(2)—O(2)	2·296 (8)	Nb(4)—O(9)	2·260 (8)
Ca(1)—O(6)	2·322 (8)	Ca(3)—O(11^{iii})	2·327 (8)
Ca(1)—O(13^{iv})	2·342 (7)	Ca(3)—O(1)	2·392 (8)
Ca(1)—O(11^{vi})	2·383 (7)	Ca(3)—O(8)	2·397 (7)
Ca(1)—O(4)	2·406 (9)	Ca(3)—O(12)	2·464 (7)
Ca(1)—O(1^{vi})	2·630 (7)	Ca(3)—O(6)	2·491 (7)
Ca(1)—O(8^{vi})	2·641 (8)	Ca(3)—O(13)	2·531 (7)
Ca(1)—O(1)	2·717 (7)	Ca(3)—O(9)	2·591 (8)
Ca(1)—O(8^{iv})	2·732 (8)	Ca(3)—O(2)	2·610 (7)
Ca(1)—O(5)	2·857 (7)	Ca(3)—O(4^{vi})	3·055 (7)
Ca(1)—O(4^{iii})	3·119 (9)	Ca(3)—O(11)	3·251 (8)
Ca(1)—O(9^{iv})	3·417 (8)	Ca(3)—O(1^{vi})	3·296 (8)
Ca(1)—O(2)	3·434 (8)	Ca(3)—O(8^{x})	3·318 (7)
Ca(2)—O(7)	2·305 (8)	Ca(4)—O(7)	2·410 (8)
Ca(2)—O(14^{iv})	2·349 (8)	Ca(4)—O(10)	2·416 (8)
Ca(2)—O(10^{ii})	2·429 (7)	Ca(4)—O(3^{ii})	2·434 (8)
Ca(2)—O(10^{iv})	2·436 (7)	Ca(4)—O(3)	2·455 (8)
Ca(2)—O(3)	2·476 (8)	Ca(4)—O(14)	2·518 (8)
Ca(2)—O(14^{i})	2·489 (7)	Ca(4)—O(12^{v})	2·681 (9)
Ca(2)—O(5)	2·534 (8)	Ca(4)—O(2)	2·833 (8)
		Ca(4)—O(9)	2·922 (7)
		Ca(4)—O(7^{i})	3·333 (8)
		Ca(4)—O(12)	3·386 (9)

Symmetry code

None	x,	y,	z	(vii)	$x+1$,	y,	z
(i)	$\bar{x}+1$,	$\bar{y}+1$,	$z+\frac{1}{2}$	(viii)	$\bar{x}+1$,	$\bar{y}+2$,	$z-\frac{1}{2}$
(ii)	$\bar{x}+1$,	$\bar{y}+1$,	$z-\frac{1}{2}$	(ix)	$\bar{x}+2$,	$\bar{y}+2$,	$z-\frac{1}{2}$
(iii)	x,	y,	$z+1$	(x)	$\bar{x}+2$,	$\bar{y}+2$,	$z+\frac{1}{2}$
(iv)	$x-1$,	y,	z	(xi)	$x+1$,	$y+1$,	z
(v)	x,	y,	$z-1$	(xii)	x,	$y+1$,	z
(vi)	$\bar{x}+1$,	$\bar{y}+2$,	$z+\frac{1}{2}$				

Discussion

The projections of the structure along the *c* and the *a* axes are shown in Figs. 1 and 2, respectively. The crystal is isomorphous with monoclinic $La_2Ti_2O_7$ (Gasperin, 1975), having Nb atoms at octahedral sites in the slabs of a perovskite-type structure. Nb—O

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34938 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

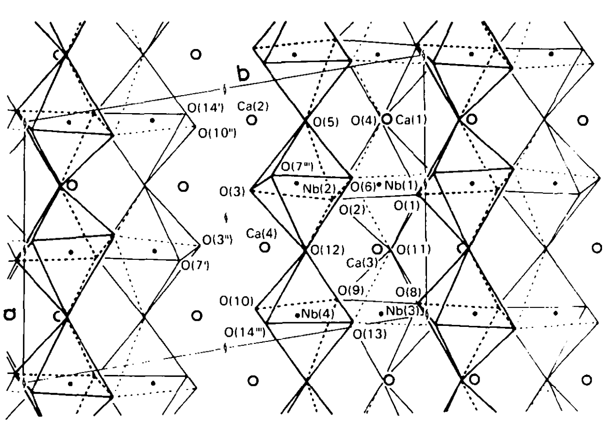

Fig. 1. The structure of monoclinic $Ca_2Nb_2O_7$ projected along the *c* axis. The numbers in parentheses refer to those of Table 3.

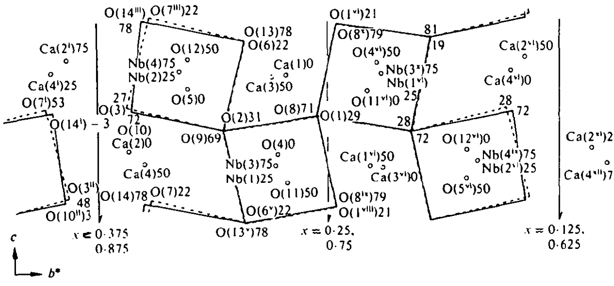

Fig. 2. The structure of monoclinic $Ca_2Nb_2O_7$ projected along the *a* axis. Heights are in units of *a*/100 above the ($\bar{4}10$) plane perpendicular to the *a* axis running through the origin.

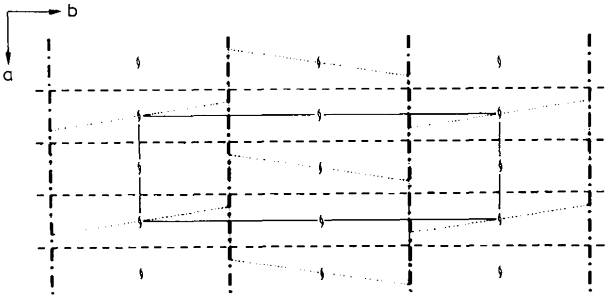

Fig. 3. The unit-cell relation between orthorhombic and monoclinic $Ca_2Nb_2O_7$. The orthorhombic and monoclinic cells are shown with solid and broken lines, respectively. The *b* and *n*-glide planes of the orthorhombic structure are also given.

distances in the $Nb(1)O_6$ and $Nb(3)O_6$ octahedra range from 1·855 (8) to 2·229 (8) Å (mean value 2·000 Å), while those in the $Nb(2)O_6$ and $Nb(4)O_6$ octahedra are between 1·794 (9) and 2·296 (8) Å (mean value 2·013 Å). Within a slab, the inner octahedra are more regular than the outer ones, as in other members of this structural family. The Ca(1) and Ca(3) atoms located in the slab are surrounded by 12 O atoms at mean distances of 2·750 and 2·727 Å, respectively. The Ca(2) and Ca(4) atoms, which lie on the boundary of the slabs connecting them, have seven and ten atoms within a distance of 3·5 Å, respectively, with mean distances of 2·431 and 2·739 Å. The structure of orthorhombic $Ca_2Nb_2O_7$ with $a = 7{\cdot}692$, $b = 26{\cdot}457$, $c = 5{\cdot}501$ Å, space group $Pbn2_1$ (Scheunemann & Müller-Buschbaum, 1974) has a relation to the present structure somewhat similar to that between orthorhombic and monoclinic pyroxenes. The orthorhombic $Ca_2Nb_2O_7$ structure is obtained by stacking the unit cells of monoclinic $Ca_2Nb_2O_7$ along the *b* axis followed by the operation of an *n* glide plane parallel to (010), as shown in Fig. 3. All the atomic positions in the orthorhombic structure derived from the monoclinic one by this symmetry operation coincide with the corresponding atomic positions reported by Scheunemann & Müller-Buschbaum (1974) within experimental error. On the other hand, the orthopyroxene structure is derived, after exchanging the *a*, *b* and *c* axes for *b*, *c* and *a*, respectively, by stacking the unit cells of clinopyroxene along the *b* axis and performing a *c* glide operation (Ito, 1950).

The structure of monoclinic $Ca_2Nb_2O_7$ is also approximately identical to those of $Sr_2Nb_2O_7$ [$a = 3{\cdot}933$, $b = 26{\cdot}726$, $c = 5{\cdot}683$ Å, $Cmc2_1$ (Ishizawa *et al.*, 1975)] and $Sr_2Ta_2O_7$ [$a = 3{\cdot}937$, $b = 27{\cdot}198$, $c = 5{\cdot}692$ Å, *Cmcm* (Ishizawa *et al.*, 1976)]. If we take monoclinic primitive cells for $Sr_2Nb_2O_7$ and $Sr_2Ta_2O_7$ in place of the orthorhombic base-centered ones, it is easily revealed that the superstructure of monoclinic $Ca_2Nb_2O_7$ is related to those of $Sr_2Nb_2O_7$ and $Sr_2Ta_2O_7$ with a doubled *a* periodicity. In $Sr_2Nb_2O_7$ and $Sr_2Ta_2O_7$ all the atom sites are on mirror planes perpendicular to the *a* axis, whereas in monoclinic $Ca_2Nb_2O_7$, atoms are shifted so as to destroy the symmetry relation of every other mirror plane within a perovskite-type slab. Since adjacent slabs are mutually shifted by an amount corresponding to the interplanar distance between mirror planes in $Sr_2Nb_2O_7$ or $Sr_2Ta_2O_7$, the surviving mirror planes in a perovskite-type slab of the present crystal are effective only within the slab, and the symmetry of the crystal is lowered to the monoclinic system. Consequently, monoclinic $Ca_2Nb_2O_7$ has local mirror planes perpendicular to the *a* axis, which explains the existence of the enantiomorphous relations between the $Nb(1)O_6$ and $Nb(3)O_6$ octahedra and between the $Nb(2)O_6$ and $Nb(4)O_6$ octahedra. Similar local mirror planes are also found in the perovskite-type slab of orthorhombic $Ca_2Nb_2O_7$. The space group *Cmcm* is the highest symmetry among those possible for the structures of $A_2B_2O_7$ compounds with perovskite-type slabs. Thus, the structure of $Sr_2Ta_2O_7$ at room temperature is considered to be an imaginary prototype for the structures of both modifications of $Ca_2Nb_2O_7$ observed at room temperature. The structural relation between the two modifications of $Ca_2Nb_2O_7$ is different from that between the pyroxenes in that the symmetries of both modifications of $Ca_2Nb_2O_7$ belong to the subgroup of the space group *Cmcm* of this imaginary prototype.

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Phosphate Ion with Three 'Symmetric' Hydrogen Bonds: The Structure of $Ca_2(NH_4)H_7(PO_4)_4.2H_2O$

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Abstract

$Ca_2(NH_4)H_7(PO_4)_4.2H_2O$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 5{\cdot}693\,(2)$, $b = 12{\cdot}299\,(4)$, $c = 6{\cdot}297\,(2)$ Å, $\alpha = 103{\cdot}98\,(2)$, $\beta = 115{\cdot}10\,(2)$, $\gamma = 84{\cdot}22\,(2)°$ [λ(Mo $K\alpha_1$) = 0·70932 Å] at room temperature with $Z = 1$. The structure was refined by the method of least squares to $R(F) = 0{\cdot}048$; $R_w(F) = 0{\cdot}050$ for 904 reflections with $F_o > 2\sigma(F_o)$. The structure contains $[CaH_2PO_4]^+$ chains held together by Ca···O bonds to form corrugated Ca–P(2)O_4 sheets analogous to those found in $Ca(H_2PO_4)_2.H_2O$ and several other calcium phosphates. Between these sheets are $[H_3(PO_4)_2]^{3-}$ ions, water molecules and $[NH_4]^+$ ions. Three of the O atoms of the P(1)O_4 group between the corrugated sheets are hydrogen bonded across three crystallographic centers of symmetry [O(11)···H···O(11); O(13)···H···O(13); O(14)···H···O(14)] forming an infinite $[H_3(PO_4)_2]_n^{3-}$ sheet structure. The water molecule is bonded to a $[CaH_2PO_4]^+$ sheet and to a $[H_3(PO_4)_2]_n^{3-}$ sheet by multiple hydrogen bonds. The $[NH_4]^+$ ion is disordered across a center of symmetry. The Ca atom is coordinated to eight O atoms with Ca···O distances in the range 2·319 to 2·687 Å.

Introduction

Gypsum, $CaSO_4.2H_2O$, contains a corrugated sheet-type structure (Wooster, 1936) which is common to a number of calcium phosphates, *e.g.* $Ca(H_2PO_4)_2.H_2O$ (Dickens & Bowen, 1971), $CaHPO_4.2H_2O$ (Curry & Jones, 1971), and $CaHPO_4$ (Dickens, Bowen & Brown, 1971). Similar sheet-type structures have been proposed for a number of other calcium phosphates, namely $CaCl(H_2PO_4).H_2O$, $Ca(NO_3)(H_2PO_4).H_2O$, $Ca_2(NH_4)H_7(PO_4)_4.2H_2O$ and $Ca_2KH_7(PO_4)_4.2H_2O$ (Brown, Smith, Lehr & Frazier, 1958). The last two, which are apparently isomorphous, were erroneously assigned the formulae $Ca_9(NH_4)_4H_{32}(PO_4)_{18}.10H_2O$ and $Ca_9K_4H_{32}(PO_4)_{18}.10H_2O$ (Flatt, Brunisholz & Chapuis-Gottreux, 1951; Flatt, Brunisholz & Hotz, 1956); the formulae $Ca_2(NH_4)H_7(PO_4)_4$ $2H_2O$ and $Ca_2KH_7(PO_4)_4.2H_2O$ were proposed by Brown *et al.* (1958).

The fact that sheet-like structures are common to several calcium phosphates indicates that these sheet-type structures are very stable in spite of the differing composition of the material between the sheets. As part of a program to study the factors contributing to the stability of the corrugated sheet and the nature of the