Structure of the Low-Temperature Variety of Calcium Sodium Orthophosphate, NaCaPO₄

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Abstract. $M_r = 158 \cdot 0$, orthorhombic, $Pn2_1a$, $a = 20 \cdot 397$ (10), $b = 5 \cdot 412$ (4), $c = 9 \cdot 161$ (5) Å, $V = 1011 \cdot 27$ Å³, $Z = 12$, $D_m = 3 \cdot 12$ (5), $D_x = 3 \cdot 12$ Mg m⁻³, λ(Mo $K\alpha$) = 0·70942 Å, $\mu = 2 \cdot 24$ mm⁻¹, $F(000) = 936$, $T = 295$ K. Final $R = 3 \cdot 8\%$ for 1234 observed reflections. The structure is related to that of β-K₂SO₄ with some orientational changes of the [PO₄] tetrahedra. It is made up of strings of Na atoms and [PO₄] tetrahedra alternating with strings of Ca atoms.

Introduction. A great number of orthophosphates have a high-temperature form with the hexagonal α-K₂SO₄-type structure. Let us quote: NaMPO₄ (M = Ca, Sr, Ba) and Na₃Ln(PO₄)₂ (Ln = rare earth) (Klement & Kresse, 1961; Vlasse, Parent, Salmon, Le Flem & Hagenmuller, 1980; Kolsi, Quarton & Freundlich, 1981).

For the Na₃Ln(PO₄)₂ compounds the high-temperature form transforms into a low-temperature variety by cationic ordering in the strings containing the Na⁺ and rare-earth ions, accompanied by a rotation of the [PO₄] tetrahedra to accommodate the new co-ordination requirements.

The study of the low-temperature phase of NaBaPO₄ does not reveal a surperstructure, but confirms a very close relationship to the α-K₂SO₄-type structure, although its symmetry seems to be monoclinic (Kolsi *et al.*, 1981).

The existence of low-temperature varieties of NaCaPO₄ and NaSrPO₄ has been previously reported, but no precise information has been given concerning their structural characteristics (Klement & Kresse, 1961; Bredig, 1942; Paques-Ledent, 1972).

Bredig (1942) had proposed for NaCaPO₄ a β-K₂SO₄-type structure, but Engel & Aalen (1976) observed superlattice reflections on the powder pattern and indexed them by isotypy with α'_L-Ca₂SiO₄, the cell parameters of which are related to those of β-K₂SO₄ by the following relations: $a \simeq 2c_{\beta\text{-K}_2\text{SO}_4}$, $b \simeq 2b_{\beta\text{-K}_2\text{SO}_4}$, $c \simeq a_{\beta\text{-K}_2\text{SO}_4}$.

In order to clarify the structural situation for low-temperature NaCaPO₄ and to provide information for better understanding of this class of materials, we decided to carry out a detailed structural determination.

Experimental. Compound prepared from a stoichiometric mixture of sodium carbonate, calcium carbonate and ammonium phosphate. Initial mixture first heated at 673 K under a nitrogen stream, then at 1223 K in air. Single crystals grown by cooling, from 1073 to 473 K at a rate of 10 Kh⁻¹, a mixture of 2 moles NaCaPO₄ and 5 moles Na₂MoO₄, the latter playing the role of a flux. Crystals separated from flux by washing in boiling water. D_m measured by pycnometry. Crystal: rectangular block, 0·08 × 0·15 × 0·03 mm fixed along **b**. Weissenberg photographs indicated orthorhombic symmetry with the extinction condition: $hk0$, $h = 2n + 1$ and $0kl$, $k + l = 2n + 1$, compatible with space group $Pn2_1a$ or $Pnma$. 30 powder-pattern general reflections used for refinement of cell parameters ($a \simeq 3a_{\beta\text{-K}_2\text{SO}_4}$, $b \simeq b_{\beta\text{-K}_2\text{SO}_4}$, $c \simeq c_{\beta\text{-K}_2\text{SO}_4}$). Enraf–Nonius CAD-3 automatic diffractometer. Lp and absorption corrections applied ($\mu R_{max} = 0 \cdot 17$). $2\theta_{max} = 80°$. h 0–30, k 0–9, l 0–16. Three standard reflections controlled for each 50 reflections measured, intensity variation ≤4% during period of measurement. 1490 total reflections, 1234 observed [$I > 3\sigma(I)$]. Deconvolution of the three-dimensional Patterson diagram in space group $Pn2_1a$ gave a satisfactory initial solution. A second harmonic generation test carried out on a powder sample proved to be positive and confirms the choice for this non-centrosymmetric space group (Jerphagnon, 1972). Refinement on F of the atomic parameters and anisotropic temperature factors using a full-matrix least-squares algorithm (*ORFLS*, Busing, Martin & Levy, 1962) led to a final R of 3·8%, ratio of data to refined variables $\simeq 7$, $w = 1$. $(\Delta/\sigma)_{av} = 0 \cdot 3$. Residual electron density peaks <0·5 e Å⁻³. No correction for secondary extinction. Atomic scattering factors from McMaster, Ker Del Grande, Mallet & Hubbel (1969).

Discussion. The final atomic coordinates are given in Table 1, interatomic distances and angles in Table 2.†

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A projection of half a unit cell on the (010) plane of the NaCaPO$_4$ structure is given in Fig. 1. For comparison the corresponding projection of the closely related β-K$_2$SO$_4$ structure is reported in Fig. 2.

Table 1. Atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j\beta_{ij}a_i^*a_j^*.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
Ca(1)	0·0011 (3)	0·2600	0·7011 (7)	0·46 (10)
Ca(2)	0·1674 (2)	0·2278 (7)	0·7943 (8)	0·55 (12)
Ca(3)	0·3356 (3)	0·2051 (6)	0·7023 (8)	0·57 (16)
Na(1)	0·0559 (7)	0·2624 (21)	0·0719 (15)	1·14 (36)
Na(2)	0·2216 (8)	0·2212 (21)	0·4277 (18)	1·58 (40)
Na(3)	0·3920 (6)	0·2368 (18)	0·0704 (15)	1·02 (37)
P(1)	0·4071 (4)	0·2539 (13)	0·4144 (10)	0·50 (19)
P(2)	0·2404 (4)	0·2226 (12)	0·0819 (9)	0·36 (16)
P(3)	0·0762 (3)	0·2238 (12)	0·4097 (9)	0·22 (14)
O(1)	0·3338 (6)	0·2761 (27)	0·4417 (19)	1·34 (48)
O(2)	0·4453 (9)	0·2588 (27)	0·5580 (20)	1·65 (42)
O(3)	0·4241 (8)	0·0140 (25)	0·3348 (17)	0·93 (41)
O(4)	0·4289 (9)	0·4769 (21)	0·3190 (19)	0·45 (40)
O(5)	0·1698 (6)	0·2758 (25)	0·0626 (17)	0·80 (41)
O(6)	0·2750 (11)	0·1705 (26)	0·9330 (22)	1·11 (50)
O(7)	0·2531 (10)	0·0093 (28)	0·1886 (22)	1·21 (54)
O(8)	0·2717 (9)	0·4650 (26)	0·1547 (20)	1·43 (51)
O(9)	0·0011 (10)	0·1720 (25)	0·4434 (17)	1·35 (49)
O(10)	0·1071 (9)	0·2686 (27)	0·5625 (20)	1·28 (41)
O(11)	0·1039 (10)	0·9974 (31)	0·3441 (23)	1·39 (59)
O(12)	0·0836 (10)	0·4553 (26)	0·3156 (22)	0·52 (51)

Table 2. Interatomic distances (Å) and angles (°) for NaCaPO$_4$

[PO$_4$] tetrahedra

P(1)—O(1)	1·52 (2)	O(1)—O(2)	2·51 (2)
P(1)—O(2)	1·53 (2)	O(1)—O(3)	2·52 (2)
P(1)—O(3)	1·53 (2)	O(1)—O(4)	2·49 (2)
P(1)—O(4)	1·56 (2)	O(2)—O(3)	2·48 (2)
⟨P(1)—O⟩	1·53	O(2)—O(4)	2·51 (2)
		O(3)—O(4)	2·51 (2)
P(2)—O(5)	1·48 (2)	O(5)—O(6)	2·52 (2)
P(2)—O(6)	1·56 (2)	O(5)—O(7)	2·51 (2)
P(2)—O(7)	1·54 (2)	O(5)—O(8)	2·47 (2)
P(2)—O(8)	1·61 (2)	O(6)—O(7)	2·54 (3)
⟨P(2)—O⟩	1·55	O(6)—O(8)	2·58 (3)
		O(7)—O(8)	2·51 (3)
P(3)—O(9)	1·59 (2)	O(9)—O(10)	2·48 (2)
P(3)—O(10)	1·55 (2)	O(9)—O(11)	2·47 (3)
P(3)—O(11)	1·48 (2)	O(9)—O(12)	2·56 (3)
P(3)—O(12)	1·53 (2)	O(10)—O(11)	2·48 (3)
⟨P(3)—O⟩	1·54	O(10)—O(12)	2·52 (3)
		O(11)—O(12)	2·53 (3)

O(1)—P(1)—O(2)	111·0 (9)	O(9)—P(3)—O(10)	104·1 (9)
O(1)—P(1)—O(3)	111·6 (9)	O(9)—P(3)—O(11)	107·5 (11)
O(1)—P(1)—O(4)	108·2 (9)	O(9)—P(3)—O(12)	110·5 (10)
O(2)—P(1)—O(3)	108·1 (9)	O(10)—P(3)—O(11)	109·9 (11)
O(2)—P(1)—O(4)	108·9 (9)	O(10)—P(3)—O(12)	109·9 (10)
O(3)—P(1)—O(4)	109·0 (9)	O(11)—P(3)—O(12)	114·4 (10)
⟨O—P(1)—O⟩	109·5 (9)	⟨O—P(3)—O⟩	109·4 (10)
O(5)—P(2)—O(6)	111·8 (10)		
O(5)—P(2)—O(7)	112·8 (10)		
O(5)—P(2)—O(8)	106·1 (9)		
O(6)—P(2)—O(7)	110·1 (10)		
O(6)—P(2)—O(8)	109·4 (9)		
O(7)—P(2)—O(8)	106·4 (9)		
⟨O—P(2)—O⟩	109·4 (10)		

Table 2 (cont.)

Calcium and sodium–oxygen polyhedra

Ca(1)—O(2)	2·48 (2)	Na(1)—O(2)	2·69 (2)
Ca(1)—O(3)	2·39 (2)	Na(1)—O(2)	2·73 (2)
Ca(1)—O(4)	2·36 (2)	Na(1)—O(2)	2·55 (2)
Ca(1)—O(9)	2·41 (2)	Na(1)—O(3)	2·60 (2)
Ca(1)—O(9)	2·59 (2)	Na(1)—O(5)	2·33 (2)
Ca(1)—O(10)	2·51 (2)	Na(1)—O(12)	2·53 (2)
Ca(1)—O(11)	2·53 (2)	Na(1)—O(3)	3·13 (2)
Ca(1)—O(12)	2·39 (2)	Na(1)—O(4)	3·01 (2)
		Na(1)—O(4)	2·80 (2)
		Na(1)—O(11)	3·04 (2)
Ca(2)—O(1)	2·79 (2)	Na(2)—O(1)	2·31 (2)
Ca(2)—O(3)	2·45 (2)	Na(2)—O(6)	2·43 (2)
Ca(2)—O(4)	2·40 (2)	Na(2)—O(7)	2·56 (2)
Ca(2)—O(5)	2·47 (2)	Na(2)—O(8)	2·50 (2)
Ca(2)—O(6)	2·56 (2)	Na(2)—O(10)	2·65 (2)
Ca(2)—O(7)	2·43 (2)	Na(2)—O(11)	2·80 (2)
Ca(2)—O(8)	2·28 (2)	Na(2)—O(6)	2·98 (2)
Ca(2)—O(10)	2·46 (2)	Na(2)—O(7)	2·90 (2)
		Na(2)—O(8)	3·01 (2)
		Na(2)—O(12)	3·25 (2)
Ca(3)—O(1)	2·42 (2)	Na(3)—O(3)	2·78 (2)
Ca(3)—O(2)	2·62 (2)	Na(3)—O(4)	2·73 (2)
Ca(3)—O(5)	2·66 (2)	Na(3)—O(6)	2·72 (2)
Ca(3)—O(6)	2·46 (2)	Na(3)—O(9)	2·26 (2)
Ca(3)—O(7)	2·50 (2)	Na(3)—O(10)	2·54 (2)
Ca(3)—O(8)	2·58 (2)	Na(3)—O(11)	2·51 (2)
Ca(3)—O(11)	2·39 (2)	Na(3)—O(7)	3·27 (2)
Ca(3)—O(12)	2·37 (2)	Na(3)—O(8)	2·85 (2)
		Na(3)—O(10)	2·88 (2)
		Na(3)—O(12)	2·83 (2)

Cation–cation distances

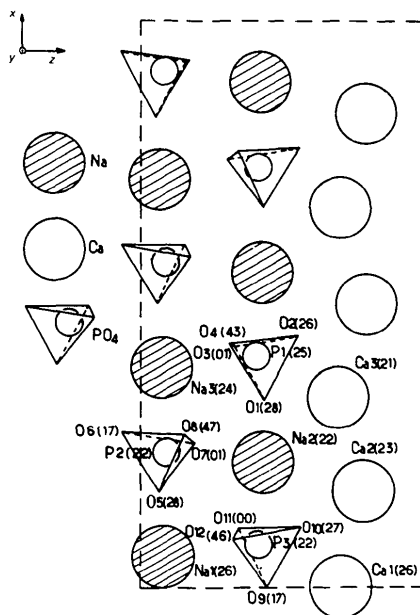|			
Ca(1)—Ca(2)	3·502 (6)	Ca(1)—Na(3)	3·58 (1)
Ca(1)—Ca(3)	3·502 (7)	Ca(1)—Na(3)	3·34 (1)
Ca(2)—Ca(3)	3·535 (8)	Ca(2)—Na(1)	3·42 (1)
Na(1)—Na(1)	3·78 (3)	Ca(2)—Na(2)	3·54 (2)
Na(2)—Na(3)	3·74 (2)	Ca(2)—Na(2)	3·57 (1)
Ca(1)—Na(1)	3·58 (1)	Ca(3)—Na(1)	3·47 (1)
Ca(1)—Na(1)	3·62 (1)	Ca(3)—Na(2)	3·43 (2)
Ca(1)—Na(1)	3·60 (1)	Ca(3)—Na(2)	3·53 (2)
		Ca(3)—Na(3)	3·57 (1)

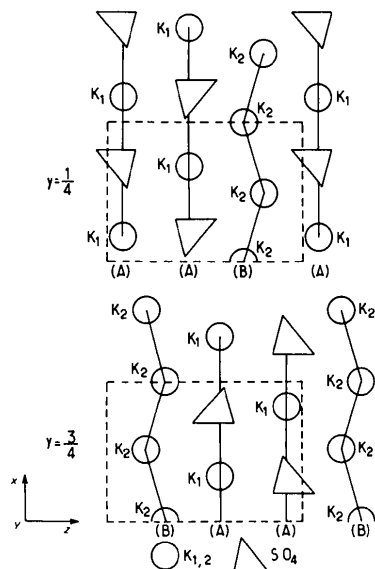Fig. 1. Projection of half a unit cell on the (010) plane of the NaCaPO$_4$ lattice.

Fig. 2. Projection of a unit cell on the (010) plane of the β-K$_2$SO$_4$ lattice.

The average P—O distances in the [PO$_4$] tetrahedra fall between 1·533 and 1·545 Å. They are in good agreement with those found for NaCd$_4$(PO$_4$)$_3$ (Ben Amara, Olazcuaga, Le Flem & Vlasse, 1979), NaMg$_4$-(PO$_4$)$_3$ (Ben Amara, Vlasse, Olazcuaga, Le Flem & Hagenmuller, 1983), NaBaPO$_4$ (Kolsi et al., 1981), which range from 1·522 to 1·549 Å. The average tetrahedral angles are in the range 109·4 to 109·5°.

The structural determination of NaCaPO$_4$ provides one more link in the chain of structures derived from the β-K$_2$SO$_4$ or the glaserite type and having the general formula $A_xB_y(XO_4)_{(x+y)/2}$. This shows the ability of the [XO$_4$] tetrahedra to change their orientation so as to accommodate the coordination requirements of the cations.

This structural type is certainly isotypic with the orthorhombic paraelectric phase of K$_2$SeO$_4$, which exists between 93 and 129·5 K (Ohama, 1974). As a consequence ferroelectric properties may be expected.

The structure can be most easily described as a superstructure of β-K$_2$SO$_4$. It is made up of two types of strings along the a axis. String A consists of alternating [PO$_4$] tetrahedra and Na atoms. String B is made up of only Ca atoms. The major difference between NaCaPO$_4$ and β-K$_2$SO$_4$ is the occurrence of three different orientations adopted here by the three independent [PO$_4$] tetrahedra. This gives rise to different coordination polyhedra for the three Ca and Na atoms and leads to the tripling of the $a_{\beta\text{-}K_2SO_4}$ parameter.

The Ca atoms are found in an eightfold co-ordination, while the Na atoms are sixfold-coordinated if we consider distances less than 2·8 Å or ten-fold-coordinated if distances up to 3·3 Å are taken into account.

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Structure d'une Deuxième Variété d'Hexathiodiphosphate(IV) d'Argent, Ag$_4$P$_2$S$_6$. Comparaison des Structures des Deux Variétés

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Abstract. $M_r = 685\cdot8$, orthorhombic, $P2_12_12_1$, $a = 13\cdot901$ (7), $b = 11\cdot073$ (6), $c = 6\cdot303$ (4) Å, $V = 970$ (2) Å^3, $Z = 4$, $D_x = 4\cdot69$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0\cdot7107$ Å, $\mu = 9\cdot1$ mm^{-1}, $F(000) = 1256$, $T = 294$ (1) K, $R = 0\cdot051$ for 1048 independent reflections $[I > 2\sigma(I)]$. This variety is isostructural with Ag$_4$P$_2$Se$_6$.