

*The unit cell and space-group of chlor-spodiosite  
(Ca<sub>2</sub>PO<sub>4</sub>Cl).*

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AS part of a study of the structure of whitlockite ( $\beta$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>) attempts were made to prepare single crystals of the mineral synthetically.<sup>1</sup> At 1180° there is a polymorphic transition from the rhombohedral  $\beta$ -form to a high-temperature monoclinic form  $\alpha$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>.<sup>2</sup> The density of the  $\alpha$ -form is 12% less than that of the  $\beta$ -form and large crystals were not found to transform without powdering. CaCl<sub>2</sub> was therefore added as a flux to see whether crystals of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> could be produced from a melt below 1180°. The melting point of pure Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> is about 1800°. In addition to chlorapatite (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Cl), a phase of composition Ca<sub>2</sub>PO<sub>4</sub>Cl was produced. This compound had been earlier observed by Cameron and McCaughey,<sup>3</sup> who identified the crystals as being closely related to the mineral spodiosite (Ca<sub>2</sub>PO<sub>4</sub>F).<sup>4</sup> A report<sup>5</sup> that spodiosite was identical with apatite appears to have been based on a specimen of altered material which was a pseudomorph of apatite after some unknown mineral. X-ray powder photographs of chlor-spodiosite and apatite are quite distinct.

The synthetic crystals were orthorhombic and exhibited the same forms, {001}, {110}, {010}, as described by Tiberg, Nordenskiöld,<sup>6</sup> and Cameron and McCaughey. (110):(1 $\bar{1}$ 0) was about 82° and flattening with the predominance of (001) was usually marked. Crystals were sometimes flattened on to (110). The hopper formation of many crystals was most striking.

<sup>1</sup> A. L. Mackay, Ph.D. Thesis, London University, 1952.

<sup>2</sup> M. A. Bredig, H. H. Franck, and H. Fuldner, Zeits. Electrochem., 1933, vol. 39, p. 959. [M.A. 6-57.]

<sup>3</sup> F. K. Cameron and W. J. McCaughey, Journ. Phys. Chem., 1911, vol. 15, p. 463.

<sup>4</sup> H. V. Tiberg, Geol. För. Förh. Stockholm, 1872, vol. 1, p. 84.

<sup>5</sup> H. Strunz, Naturwiss., 1939, vol. 27, p. 423. [M.A. 7-494.]

<sup>6</sup> G. Nordenskiöld, Geol. För. Förh. Stockholm, 1893, vol. 15, p. 460.

The refractive indices were found to be  $\alpha$  1.65<sub>0</sub>,  $\beta$  1.66<sub>3</sub>,  $\gamma$  1.67<sub>0</sub>. The acute and obtuse bisectrix figures confirmed the negative optic sign;  $2V$   $75^\circ \pm 5^\circ$  (measured). The optic orientation is  $\alpha = b$ ,  $\beta = a$ ,  $\gamma = c$ . Larsen<sup>1</sup> gives the indices  $\alpha$  1.663,  $\beta$  1.674,  $\gamma$  1.699 with the optic sign positive for the natural spodiosite ( $\text{Ca}_2\text{PO}_4\text{F}$ ).

Cameron and McCaughey give the refractive indices of chlor-spodiosite as  $\alpha$  1.649,  $\beta$  1.665,  $\gamma$  1.670 and state that the birefringence is positive, that  $c$  is the acute bisectrix and that  $a$  is the obtuse bisectrix. They also say that the prism angle  $(110):(1\bar{1}0)$  is  $82^\circ$ , presumably implying that  $(110):(1\bar{1}0) = 98^\circ$  (the  $a$  and  $b$  axes are interchanged with respect to those used in this paper). It will be observed that their optic sign is inconsistent with their refractive indices and appears to have been determined from the obtuse bisectrix figure. If this is so, then their optical properties agree with those found by the present author.

From precession camera photographs the unit-cell dimensions were measured as  $a$  6.17,  $b$  6.89,  $c$  10.74 Å. Using the measured density of 3.03 g./c.c. (Cameron and McCaughey, 3.041) the calculated number  $Z$  of formula units per cell is  $3.95_0 \approx 4$ . Extinctions in the X-ray pattern are characteristic of the diffraction symbol  $P2/b2_1/c2_1/m$ . The space-group is therefore probably  $Pbcm$  or  $Pca2_1$ . As a Giebe-Scheibe test for piezoelectricity gave negative results the centred group  $Pbcm$  is to be preferred. From goniometric measurements Nordenskiöld obtained for the axial ratios of natural spodiosite  $a:b:c = 0.893:1:1.584$ . The X-ray measurements above give  $0.896:1:1.559$  as the corresponding values for the chlor-spodiosite, confirming the similarity of the two varieties.

These orthorhombic cell dimensions provide some justification for the inclusion by Dana of spodiosite in the wagnerite group. Wagnerite itself ( $\text{Mg}_2\text{PO}_4\text{F}$ ) is monoclinic with space-group  $P2_1/c$  and has dimensions  $a$  11.90,  $b$  12.51,  $c$  9.63 kX,  $\beta$   $108^\circ 07'$ ;  $Z$  16 and a density of about 3.07–3.14 g./c.c. Mg may be replaced by ferrous iron or Mn, F by OH, and P by As, altering the dimensions and density slightly. As these substitutions are possible, it would seem that the structure has considerable stability and probably remains substantially unchanged when Ca and Cl are introduced, although these ions are somewhat larger than the corresponding ions in wagnerite. It will be noted that the  $a$  and  $b$  dimensions of wagnerite are nearly twice those of chlor-spodiosite and the  $c$  dimension is slightly less, while  $Z$  is correspondingly

<sup>1</sup> E. S. Larsen, Bull. U.S. Geol. Surv., 1921, no. 679, pp. 136, 223.

four times as large. It is plausible that the increase in the size of the ions may simplify the structure. There is also a resemblance to the orthorhombic members of the olivenite ( $\text{Cu}_2(\text{AsO}_4)(\text{OH})$ ) and descloizite ( $\text{Pb}(\text{Zn}, \text{Cu})\text{VO}_4(\text{OH})$ ) groups. No members of these groups containing chlorine ions are known, so that very close relationships are not necessarily expected.

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