Swiss National Science Foundation under project No. 2.250-0.79.

References

BRUNNER, G. O. (1977). *Acta Cryst.* A**33**, 226–227.
BRUNNER, G. O. & SCHWARZENBACH, D. (1971). *Z. Kristallogr.* **133**, 127–133.
BRUZZONE, G., FORNASINI, M. L. & MERLO, F. (1971). *J. Less-Common Met.* **22**, 253–264.
CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
FRANK, F. C. & KASPER, J. S. (1958). *Acta Cryst.* **11**, 184–190.
IANDELLI, A. & PALENZONA, A. (1973). *Rev. Chim. Minér.* **10**, 303–308.
IANDELLI, A. & PALENZONA, A. (1974). *J. Less-Common Met.* **38**, 1–7.
IANDELLI, A. & PALENZONA, A. (1975). *J. Less-Common Met.* **43**, 205–209.
International Tables for X-ray Crystallography (1967). Vol. II. Birmingham: Kynoch Press.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
LE ROY, J., MOREAU, J.-M., PACCARD, D. & PARTHÉ, E. (1979). *Acta Cryst.* B**35**, 1437–1439.
LE ROY, J., PACCARD, D. & MOREAU, J.-M. (1980). *J. Less-Common Met.* In the press.
LOEBICH, JR O. & RAUB, E. (1976). *J. Less-Common Met.* **46**, 7–15.
MOREAU, J.-M. & PACCARD, D. (1976). *Acta Cryst.* B**32**, 1654–1657.
O'KEEFFE, M. (1979). *Acta Cryst.* A**35**, 772–775.
PALENZONA, A. (1979). *J. Less-Common Met.* **66**, P27–P33.
SANJINES-ZEBALLOS, R., CHABOT, B. & PARTHÉ, E. (1980). *J. Less-Common Met.* In the press.
XRAY system (1976). Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
YVON, K., JEITSCHKO, W. & PARTHÉ, E. (1977). *J. Appl. Cryst.* **10**, 73–74.

Acta Cryst. (1980). B**36**, 1634–1636

Structure of Potassium Arsenate $K_5As_3O_{10}$

BY J. HORNSTRA AND H. VERWEIJ

Philips Research Laboratories, Eindhoven, The Netherlands

(*Received* 25 *September* 1979; *accepted* 25 *February* 1980)

Abstract. $K_5As_3O_{10}$, orthorhombic, $P2_12_12_1$, $a = 7·98\ (1)$, $b = 7·97\ (1)$, $c = 19·30\ (2)$ Å, $V = 1227·5$ Å^3, $Z = 4$, $D_m = 3·06$, $D_c = 3·14$ Mg m^{-3}, μ(Mo $K\alpha$, $\lambda = 0·7107$ Å) = 10·5 mm^{-1}. The structure was solved by Patterson methods from X-ray single-crystal data. For 912 independent intensity data the final $R = 0·04$. Each As atom is tetrahedrally surrounded by four O atoms. Groups of three corner-sharing tetrahedra form strongly bent chains. The coordination number of the K atoms varies from six to nine. Tetragonal pseudosymmetry may lead to twinning.

Introduction. Structural data on potassium arsenates are needed for a study on As-containing silicate glasses (Verweij, 1979). Condensed alkali arsenates generally contain chains or rings of corner-sharing AsO_4 tetrahedra. $(LiAsO_3)_x$ (von Hilmer & Dornberger-Schiff, 1956) and $(NaAsO_3)_x$ (Liebau, 1956) contain chains of infinite length, whereas $Na_4As_2O_7$ (Leung & Calvo, 1973) contains pyroarsenate groups, built up from two AsO_4 tetrahedra.

Compounds similar to the title compound are $Na_5As_3O_{10}$ (Thilo & Winkler, 1966) of unknown crystal structure, $Na_5P_3O_{10}$ (Corbridge, 1960) containing stretched chains of three tetrahedra, and $H_5As_3O_{10}$ (Jost, Worzala & Thilo, 1966) which contains ribbons consisting of AsO_4 tetrahedra and AsO_6 octahedra.

The phase diagram of the K_2O–As_2O_5 system (Levin, Robbins & McMurdie, 1964) shows four compounds which are stable at room temperature: α-K_3AsO_4, $K_4As_2O_7$, $K_5As_3O_{10}$ and γ-$KAsO_3$. The title compound, $K_5As_3O_{10}$, melts incongruently at 903 K.

Single crystals were grown from a melt in a Pt–10% Rh crucible by cooling from 1073 K at a rate of 0·14 K min^{-1}. The composition of the melt was 58 mol% K_2O and 42 mol% As_2O_5, which is between that of $K_5As_3O_{10}$ and the eutectic between γ-$KAsO_3$ and $K_5As_3O_{10}$ (Levin, Robbins & McMurdie, 1964), so that the title compound was the primary crystalline phase on cooling. The cooled mixture consisted of microscopic needles of γ-$KAsO_3$ (Thilo & Dostál, 1959; Grunze, Dostál & Thilo, 1959) and transparent, highly imperfect crystals of $K_5As_3O_{10}$. The crystals were very hygroscopic and had to be handled in a glove bag filled with nitrogen (I^{2}R, Cheltenham, PA, USA). An irregular beam-shaped crystal of dimensions 0·32 × 0·20 × 0·08 mm was sealed in a glass capillary

0567-7408/80/071634-03$01.00
© 1980 International Union of Crystallography

and mounted on a PW 1100 computer-controlled four-circle diffractometer (Hornstra & Vossers, 1973). The crystal appeared homogeneous when inspected with a polarization microscope.

The reflections were obtained in ω scans with a stationary detector. Many reflections showed a satellite at about 0·5° from the main reflection with an intensity about one tenth that of the main reflection. These satellites were included in the integrated intensity. The similarity of the a and b axes suggested tetragonal symmetry; in addition, many hkl–khl pairs had similar intensities. The 130 reflection, however, was three times stronger than the 310. This showed the structure to be orthorhombic.

Owing to the irregular shape of the specimen, an exact absorption correction was impossible. Therefore, the intensity of the $\bar{1}23$ reflection, a plane almost perpendicular to the φ axis, was measured at various azimuths. This showed how the intensity varied with φ and all intensities were corrected correspondingly. After this procedure the differences between symmetry-related reflections were comparable to the final R factor. By averaging over symmetry-related reflections, 912 independent intensity data were obtained from 3796 individual measurements up to $\theta = 22°$. The computer programs used for structure determination were by P. B. Braun, J. Hornstra and J. I. Leenhouts (Philips Research Laboratories, Eindhoven, The Netherlands). The structure was solved from the Patterson function which showed pseudotetragonal symmetry. In the least-squares refinement of the parameters the sum of $w(F_o - F_c)^2$ was minimized. The weighting system used was that described by Braun, Hornstra & Leenhouts (1970). Although the starting set of parameters of all K and As atoms had tetragonal symmetry (space group $P4_12_12$ with 4_1 along $\frac{1}{4}0z$), full-matrix refinement in $P2_12_12_1$ started without problems. A difference-Fourier synthesis gave all O positions. These positions showed clearly that the crystal was not tetragonal.

Table 1. *Atomic parameters: fractional coordinates* ($\times 10^4$) *and isotropic thermal parameters*

Estimated standard deviations are in parentheses.

	x	y	z	B (Å^2)
As(1)	720 (1)	3253 (2)	1242 (1)	1·28 (5)
As(2)	4730 (1)	2778 (2)	1471 (1)	1·15 (6)
As(3)	183 (2)	7294 (2)	1060 (1)	1·33 (6)
K(1)	4930 (3)	2425 (3)	3769 (2)	1·96 (9)
K(2)	2646 (4)	64 (4)	54 (1)	2·12 (10)
K(3)	2451 (4)	6 (3)	2526 (1)	1·96 (10)
K(4)	2526 (4)	4581 (4)	−296 (1)	2·52 (12)
K(5)	2261 (4)	5273 (4)	2669 (1)	2·27 (11)
O(1)	127 (11)	2536 (11)	476 (5)	2·8 (3)
O(2)	317 (11)	2255 (11)	1955 (5)	3·1 (4)
O(3)	396 (11)	7133 (11)	197 (4)	2·8 (3)
O(4)	181 (10)	217 (10)	3615 (5)	2·8 (3)
O(5)	1617 (10)	3168 (11)	3725 (5)	3·1 (4)
O(6)	1852 (11)	7933 (12)	1468 (5)	3·5 (5)
O(7)	2848 (9)	3822 (11)	1180 (5)	3·0 (4)
O(8)	3841 (11)	9049 (11)	3847 (5)	3·3 (4)
O(9)	4640 (10)	2812 (10)	2331 (4)	1·9 (3)
O(10)	4731 (11)	848 (11)	1172 (5)	3·4 (3)

The introduction of anisotropic thermal parameters only reduced the reliability factor from 4·2 to 3·8% and was therefore considered not to be significant. The final parameters are given in Table 1.* Because pseudosymmetry favours twinning, the list of observed and calculated structure factors and the final difference-Fourier map were carefully inspected since X-ray photographs would not reveal this type of twinning. They showed that, at most, 10% of the specimen was in the twinned orientation. Because of this, some parameters may be in error by slightly more than 3σ.

Discussion. The structure may be described in terms of a body-centred subcell with dimensions $a/2$, $b/2$, $c/4$. If the origin is chosen at $\frac{1}{4}00$, all corners of the subcell are occupied by K atoms (see Fig. 1). One quarter of these subcells have K(1) at their centres; the others contain As. O atoms are found near the centres of the faces of these subcells.

Atom K(1) is surrounded by six O atoms (see Table 2), forming a nearly regular octahedron. K(2) and K(3) have eight O neighbours forming a distorted dodecahedron. The six O atoms around K(4) form an irregular octahedron and K(5) has nine O atoms at a distance less than 3·35 Å.

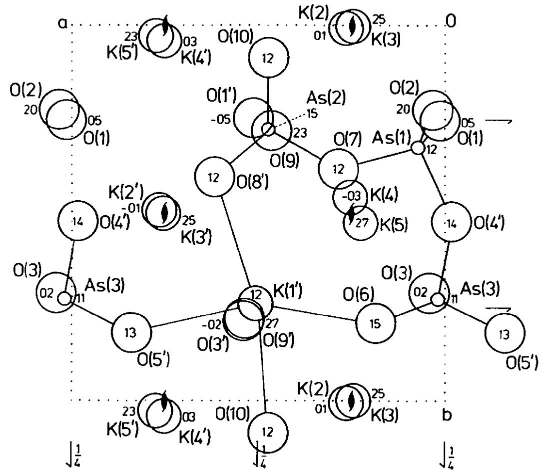

Fig. 1. Projection on (001) of the atoms with $0 < z < 0{\cdot}27$; the z coordinates are given in units of 0·01.

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35164 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Short interatomic distances* (Å)

E.s.d.'s of distances involving O are 0·01 Å.

As(1)—O(2)	1·62	K(2)—O(8)	2·71	K(4)—O5	2·68
As(1)—O(1)	1·65	K(2)—O(10)	2·80	K(4)—O(1)	2·70
As(1)—O(4)	1·75	K(2)—O(3)	2·85	K(4)—O(3)	2·82
As(1)—O(7)	1·76	K(2)—O(1)	2·93	K(4)—O(10)	2·82
As(2)—O(10)	1·64	K(2)—O(1)	2·94	K(4)—O(1)	2·92
As(2)—O(8)	1·64	K(2)—O(3)	2·96	K(4)—O(7)	2·92
As(2)—O(9)	1·66	K(2)—O(6)	3·28	K(5)—O(5)	2·68
As(2)—O(7)	1·81	K(2)—O(4)	3·28	K(5)—O(2)	2·69
As(3)—O(6)	1·63	K(3)—O(6)	2·67	K(5)—O(9)	2·81
As(3)—O(5)	1·66	K(3)—O(2)	2·71	K(5)—O(7)	3·13
As(3)—O(3)	1·68	K(3)—O(4)	2·78	K(5)—O(4)	3·15
As(3)—O(4)	1·79	K(3)—O(9)	2·86	K(5)—O(6)	3·16
K(1)—O(6)	2·64	K(3)—O(8)	2·88	K(5)—O(2)	3·18
K(1)—O(5)	2·71	K(3)—O(9)	2·92	K(5)—O(9)	3·20
K(1)—O(10)	2·74	K(3)—O(10)	3·25	K(5)—O(10)	3·31
K(1)—O(3)	2·79	K(3)—O(2)	3·27	As(1)—As(2)	3·25
K(1)—O(9)	2·80			As(1)—As(3)	3·27
K(1)—O(8)	2·83				

The As atoms are surrounded by four O atoms in almost regular tetrahedra, forming chains of three by sharing corners (see Fig. 1). The angles As(1)—O(7)—As(2) and As(1)—O(4)—As(3) have normal values of 131·4 and 134·9° respectively. For the non-bridging O atoms a mean As—O distance of 1·65 Å is found, and for the bridging O atoms 1·78 Å, in agreement with other arsenates. The strong bending of the chain is shown by the angle As(2)—As(1)—As(3), which is only 105·0°, compared with a corresponding angle of 173° in the chains of $Na_5P_3O_{10}$ (Corbridge, 1960).

References

BRAUN, P. B., HORNSTRA, J. & LEENHOUTS, J. I. (1970). *Acta Cryst.* B**26**, 352–356.

CORBRIDGE, D. E. C. (1960). *Acta Cryst.* **13**, 263–269.

GRUNZE, I., DOSTÁL, K. & THILO, E. (1959). *Z. Anorg. Allg. Chem.* **302**, 221–229.

HILMER, W. VON & DORNBERGER-SCHIFF, K. (1956). *Acta Cryst.* **9**, 87–88.

HORNSTRA, J. & VOSSERS, H. (1973). *Philips Tech. Rev.* **33**, 61.

JOST, K. H., WORZALA, H. & THILO, E. (1966). *Acta Cryst.* **21**, 808–813.

LEUNG, K. Y. & CALVO, C. (1973). *Can. J. Chem.* **51**, 2082–2088.

LEVIN, E. M., ROBBINS, C. R. & MCMURDIE, F. (1964). *Phase Diagrams for Ceramists.* Part 1, p. 88. Columbus, Ohio: The American Ceramic Society.

LIEBAU, F. (1956). *Acta Cryst.* **9**, 811–817.

THILO, E. & DOSTÁL, K. (1959). *Z. Anorg. Allg. Chem.* **298**, 100–115.

THILO, E. & WINKLER, A. (1966). *Monatsber. Dtsch. Akad. Wiss. Berlin*, **8**, 301–304.

VERWEIJ, H. (1979). *J. Am. Ceram. Soc.* **62**, 450–455.

Acta Cryst. (1980). B**36**, 1636–1639

Structure of Hydroxyellestadite

By K. SUDARSANAN

Engineering Experiment Station, Georgia Institute of Technology, Atlanta, Georgia 30332, *USA*

(*Received* 15 *October* 1979; *accepted* 3 *March* 1980)

Abstract. $Ca_{10}(SiO_4)_3(SO_4)_3(OH,Cl,F)_2$, monoclinic, $P2_1/m$, with $a = 9{\cdot}476\,(2)$, $b = 9{\cdot}508\,(2)$, $c = 6{\cdot}919\,(1)$ Å, and $\gamma = 119{\cdot}53\,(2)°$ (*c* is taken as the unique axis because of the relation to the hexagonal apatite structure). In hydroxyellestadite, a main constituent of normal apatite, PO_4, is completely replaced by SiO_4 and SO_4 groups without compensating substitutions elsewhere in the structure. The structure resembles that of apatite. Least-squares refinement with 3040 independent diffractometer-measured X-ray intensities showed three different sizes for tetrahedral groups (average Si,S to O distances 1·52, 1·54 and 1·57 Å), indicating a preferential substitution of SO_4 and SiO_4 for different PO_4 groups but not a complete substitution by one atom at any particular site.

Introduction. The ellestadite series, the sulfate silicate apatites showing substitutions for phosphorus, have only been subjected to limited structural analysis. Wilkeite, a mineral from Southern California containing approximately 12% SO_3, 9% SiO_2 and 21% P_2O_5, has been assigned to the apatite group by Eakle & Rogers (1914) on the basis of its crystallographic, physical and optical properties. Ellestadite and other sulfate silicate apatites containing halogens and minor amounts of CO_3 and PO_4 were first described by McConnel (1937, 1938). It is one of the skarn minerals from Crestmore, Riverside County, California. Hydroxyellestadite and fluorellestadite have been synthesized by Dihn & Clement (1942) and Takemato & Kato (1968). Harada, Nagashima, Nakao & Kato (1971) reported the existence of the mineral hydroxyellestadite in the Chichibu Mine, Saitema Prefecture, Japan. From a chemical analysis they have proposed the formula $(Ca_{9\cdot656}Na_{0\cdot109}Sr_{0\cdot027}Fe_{0\cdot026}K_{0\cdot615}Mn_{0\cdot001})(SiO_4)_{2\cdot860}(SO_4)_{2\cdot675}(CO_3OH)_{0\cdot370}(PO_4)_{0\cdot002}(OH)_{1\cdot877}Cl_{0\cdot255}F_{0\cdot146}$. The importance of this mineral is that it is the only mineral reported in which PO_4, a main constituent of

0567-7408/80/071636-04$01.00 © 1980 International Union of Crystallography