

## References

- BAUR, W. H. (1970). *Handbook of Geochemistry*, edited by K. H. WEDEPOHL. Berlin: Springer.
- BAUR, W. H. (1972). *Acta Cryst.* B28, 1456–1465.
- BAUR, W. H. (1978). *Acta Cryst.* B34, 1751–1756.
- BAUR, W. H., BIENIOK, A., SHANNON, R. D. & PRINCE, E. (1988). *Z. Kristallogr.* In the press.
- BAUR, W. H. & FISCHER, R. X. (1986). *Adv. X-ray Anal.* 29, 131–142.
- BAUR, W. H., FISCHER, R. X. & SHANNON, R. D. (1988). In *Innovation in Zeolite Materials Science. Studies in Surface Science and Catalysis*, edited by P. J. GROBET, W. J. MORTIER, E. F. VANSANT & G. SCHULZ-EKLOFF, pp. 281–292. Amsterdam, Oxford, New York, Tokyo: Elsevier.
- BAUR, W. H., FISCHER, R. X., SHANNON, R. D., STALEY, R. H., VEGA, A. J., ABRAMS, L., CORBIN, D. R. & JORGENSEN, J. D. (1987). *Z. Kristallogr.* 179, 281–304.
- BAUR, W. H. & OHTA, T. (1982). *Acta Cryst.* B38, 390–401.
- BAUR, W. H., WENNINGER, G. & ROY, S. D. (1986). *SADIAN86*. Univ. Frankfurt, Federal Republic of Germany.
- FISCHER, R. X. (1985). *J. Appl. Cryst.* 18, 258–262.
- FISCHER, R. X., BAUR, W. H., SHANNON, R. D. & STALEY, R. H. (1987). *J. Phys. Chem.* 91, 2227–2230.
- FISCHER, R. X., BAUR, W. H., SHANNON, R. D., STALEY, R. H., ABRAMS, L., VEGA, A. J. & JORGENSEN, J. D. (1988). *Acta Cryst.* B44, 321–334.
- FISCHER, R. X., BAUR, W. H., SHANNON, R. D., STALEY, R. H., VEGA, A. J., ABRAMS, L. & PRINCE, E. (1986a). *J. Phys. Chem.* 90, 4414–4423.
- FISCHER, R. X., BAUR, W. H., SHANNON, R. D., STALEY, R. H., VEGA, A. J., ABRAMS, L. & PRINCE, E. (1986b). *Zeolites*, 6, 378–387.
- FLANK, W. H. (1977). In *Molecular Sieves—II. Am. Chem. Soc. Symp. Ser. No. 40*, edited by J. R. KATZER, pp. 43–52. Washington, DC: American Chemical Society.
- International Tables for Crystallography* (1983). Vol. A, pp. 653, 703. Dordrecht: Kluwer Academic Publishers.
- JORGENSEN, J. D. & FABER, J. (1983). *Proc. 6th Meet. Int. Colloq. Adv. Neutron Sources*. Report ANL-82-80, pp. 105–114. Argonne National Laboratory, IL, USA.
- KEANE, M., SONNICHSEN, G. C., ABRAMS, L., CORBIN, D. R., GIER, T. E. & SHANNON, R. D. (1987). *Appl. Catal.* 32, 361–366.
- KHAN, A. A. & BAUR, W. H. (1972). *Acta Cryst.* B28, 683–693.
- KOESTER, L. (1977). *Springer Tracts Mod. Phys.* 80, 1–55.
- MCCUSKER, L. B. (1984). *Zeolites*, 4, 51–55.
- PARISE, J. B., ABRAMS, L., GIER, T. E., CORBIN, D. R., JORGENSEN, J. D. & PRINCE, E. (1984). *J. Phys. Chem.* 88, 2303–2307.
- PARISE, J. B., GIER, T. E., CORBIN, D. R. & COX, D. E. (1984). *J. Phys. Chem.* 88, 1635–1640.
- PARISE, J. B. & PRINCE, E. (1983). *Mater. Res. Bull.* 18, 841–852.
- PRINCE, E. (1980). *Natl Bur. Stand. Tech. Note* No. 1117, p. 8.
- PRINCE, E. & SANTORO, A. (1980). *Natl Bur. Stand. Tech. Note* No. 1117, pp. 11–12.
- RIETVELD, H. M. (1969). *J. Appl. Cryst.* 2, 65–71.
- ROBSON, H. E., SHOEMAKER, D. P., OGILVIE, R. A. & MANOR, P. C. (1973). In *Molecular Sieves. Advances in Chemistry Series* No. 121, edited by W. M. MEIER & J. B. UYTTERHOEVEN, pp. 106–115. Washington, DC: American Chemical Society.
- ROTELLA, F. J. (1982). *Users Manual for Rietveld Analysis of Time-of-Flight Neutron Powder Data at IPNS*. Intense Pulsed Neutron Source, Argonne, IL, USA.
- SHANNON, R. D., KEANE, M., ABRAMS, L., STALEY, R. H., GIER, T. E., CORBIN, D. R. & SONNICHSEN, G. C. (1988). *J. Catal.* 114, 8–16.
- STUCKY, G. D., EDDY, M. M., PRINCE, E., ABRAMS, L., CORBIN, D. R. & JONES, G. (1986). *Proc. Am. Crystallogr. Assoc. Meet.* Abstr. No. 14, p. 19.
- UDOVIC, T. J., CAVANAGH, R. R., RUSH, J. J., WAX, H. J., STUCKY, G. D., JONES, G. A. & CORBIN, D. R. (1987). *J. Phys. Chem.* 91, 5968–5973.
- VEGA, A. J. & LUZ, Z. (1987). *J. Phys. Chem.* 91, 365–373.
- VON DREELE, R. B., JORGENSEN, J. D. & WINDSOR, C. G. (1982). *J. Appl. Cryst.* 15, 581–589.

*Acta Cryst.* (1989). C45, 989–991

## Structure of a Diphosphate of Trivalent Molybdenum, $\text{RbMoP}_2\text{O}_7$

BY D. RIOU, A. LECLAIRE, A. GRANDIN AND B. RAVEAU

*Laboratoire de Cristallographie et Sciences des Matériaux, CRISMAT – ISMRa, Université de Caen, Campus 2, Boulevard du Maréchal Juin, 14032 Caen CEDEX, France*

(Received 6 October 1988; accepted 3 January 1989)

**Abstract.** Molybdenum rubidium diphosphate,  $\text{MoRbP}_2\text{O}_7$ ,  $M_r = 355.35$ , monoclinic,  $P2_1/c$ ,  $a = 7.5237$  (6),  $b = 10.3537$  (8),  $c = 8.3998$  (8) Å,  $\beta = 105.8321$  (69)°,  $V = 629.51$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 3.749$  g cm<sup>-3</sup>,  $\lambda(\text{Mo K}\alpha) = 0.71069$  Å,  $\mu = 106$  cm<sup>-1</sup>,  $F(000) = 660$ ,  $T = 298$  K,  $R = 0.039$ ,  $wR = 0.054$  for 2792 independent reflections with  $\sigma(I)/I \leq 0.333$ . The framework is built up from corner-sharing  $\text{MoP}_2\text{O}_{11}$  units which delimit cages where Rb atoms are located. These cavities are

interconnected, leading to an intersecting tunnel structure.

**Introduction.** The investigation of the systems  $A\text{—Mo—P—O}$  ( $A = \text{Na, K, Rb, Cs}$ ) allowed several alkaline molybdenum diphosphates with the general formulation  $A\text{MoP}_2\text{O}_7$  to be isolated, in which molybdenum exhibits the trivalent oxidation state. The diphosphates  $\text{KMoP}_2\text{O}_7$  (Leclaire, Borel, Grandin & Raveau, 1989) and  $\text{CsMoP}_2\text{O}_7$  (Lii & Haushalter, 1987) are isotopic

Table 1. Positional parameters and their e.s.d.'s

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub> * (Å <sup>2</sup> )
Mo	0.23554 (4)	0.60004 (3)	0.75928 (4)	0.376 (3)
Rb	0.18674 (6)	0.31780 (5)	0.05344 (6)	1.427 (7)
P(1)	0.4375 (1)	0.6358 (1)	0.1904 (1)	0.49 (1)
P(2)	0.1309 (1)	0.9015 (1)	0.8272 (1)	0.50 (1)
O(1)	0.3325 (4)	0.5645 (3)	0.3102 (4)	1.15 (5)
O(2)	0.0810 (4)	0.7326 (3)	0.2546 (4)	1.05 (5)
O(3)	0.6312 (4)	0.5796 (3)	0.2361 (4)	1.28 (5)
O(4)	0.1378 (4)	0.5914 (3)	0.5050 (4)	1.48 (5)
O(5)	0.3242 (5)	0.6047 (4)	0.0182 (4)	1.68 (6)
O(6)	0.0017 (4)	0.4996 (3)	0.2222 (4)	1.07 (5)
O(7)	0.4491 (4)	0.7786 (3)	0.2350 (4)	1.13 (5)

\* Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:

$$\frac{1}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + abc\cos\gamma B(1,2) + a\cos\beta B(1,3) + b\cos\alpha B(2,3)]$$

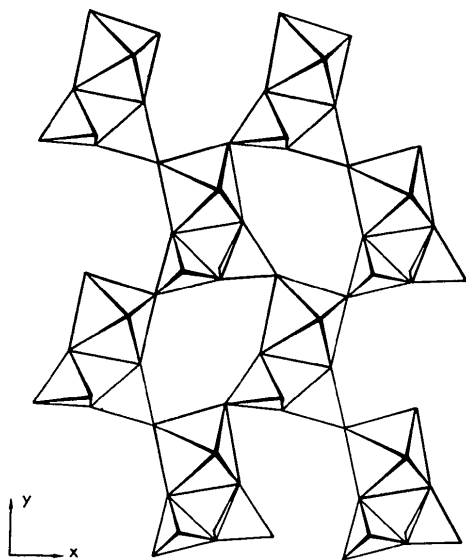


Fig. 1. Layer with heptagonal windows.

with the iron diphosphate  $\text{KFeP}_2\text{O}_7$  (Riou, Labbé & Goreaud, 1988) and aluminium diphosphate  $\text{KAlP}_2\text{O}_7$  (Hok-Nam & Calvo, 1973), and are characterized by an intersecting tunnel structure different from that of the sodium diphosphates  $\text{NaMoP}_2\text{O}_7$  (Leclaire, Borel, Grandin & Raveau, 1988a) and  $\text{Na}_x\text{MoP}_2\text{O}_7$  ( $0.25 \leq x \leq 0.50$ ) (Leclaire, Borel, Grandin & Raveau, 1988b). The present paper deals with the crystal structure of  $\text{RbMoP}_2\text{O}_7$ .

**Experimental.** Crystals were synthesized from a mixture of  $(\text{NH}_4)_2\text{HPO}_4$ ,  $\text{MoO}_3$  and  $\text{Rb}_2\text{CO}_3$  in appropriate ratios, first heated in a platinum crucible for one hour at 673 K to decompose entirely the phosphate and carbonate, then an adequate amount of Mo was added and the product was ground up and placed in an

Table 2. Bond lengths (Å) and angles (°)

PO <sub>4</sub> tetrahedra				
P(1)	O(1)	O(3)	O(5)	O(7)
O(1)	1.617 (2)	2.495 (3)	2.471 (3)	2.527 (3)
O(3)	105.4 (1)	1.518 (2)	2.538 (3)	2.473 (3)
O(5)	104.8 (1)	114.5 (2)	1.500 (2)	2.551 (3)
O(7)	107.2 (1)	108.9 (1)	115.2 (1)	1.522 (2)
P(2)	O(1 <sup>v</sup> )	O(2 <sup>v</sup> )	O(4 <sup>v</sup> )	O(6 <sup>v</sup> )
O(1 <sup>v</sup> )	1.601 (2)	2.519 (3)	2.493 (3)	2.487 (3)
O(2 <sup>v</sup> )	107.5 (1)	1.522 (2)	2.501 (3)	2.482 (3)
O(4 <sup>v</sup> )	107.8 (1)	112.7 (1)	1.483 (2)	2.504 (3)
O(6 <sup>v</sup> )	105.8 (1)	109.5 (1)	113.1 (1)	1.518 (2)

MoO<sub>6</sub> octahedron

Mo	O(2 <sup>v</sup> )	O(3 <sup>v</sup> )	O(4)	O(5 <sup>ii</sup> )	O(6 <sup>iv</sup> )	O(7 <sup>v</sup> )
O(2 <sup>v</sup> )	2.081 (2)	3.701 (4)	2.895 (3)	2.980 (3)	2.852 (3)	2.859 (3)
O(3 <sup>v</sup> )	174.46 (8)	2.109 (2)	2.971 (3)	2.951 (4)	2.941 (3)	3.197 (3)
O(4)	88.7 (1)	90.8 (1)	2.062 (2)	3.436 (5)	2.924 (3)	2.926 (3)
O(5 <sup>ii</sup> )	91.1 (1)	89.2 (1)	177.5 (1)	2.094 (2)	2.925 (3)	3.037 (4)
O(6 <sup>iv</sup> )	85.92 (9)	88.55 (9)	89.16 (9)	88.3 (1)	2.104 (2)	4.188 (5)
O(7 <sup>v</sup> )	86.46 (8)	99.06 (8)	89.50 (9)	93.0 (1)	172.29 (9)	2.093 (2)

RbO<sub>10</sub> polyhedron

Rb—O(1)	3.330 (3)	Rb—O(4 <sup>viii</sup> )	3.323 (3)
Rb—O(2 <sup>iii</sup> )	2.861 (2)	Rb—O(5)	3.185 (3)
Rb—O(2 <sup>viii</sup> )	3.035 (2)	Rb—O(6)	2.927 (2)
Rb—O(3 <sup>iv</sup> )	3.276 (2)	Rb—O(6 <sup>iii</sup> )	3.025 (2)
Rb—O(3 <sup>vi</sup> )	3.125 (2)	Rb—O(7 <sup>vii</sup> )	2.859 (2)

Symmetry code: (i)  $-x, -y, -z$ ; (ii)  $x, y, z+1$ ; (iii)  $-x, 1-y, -z$ ; (iv)  $-x, 1-y, 1-z$ ; (v)  $x, 1.5-y, 0.5+z$ ; (vi)  $1-x, 1-y, -z$ ; (vii)  $1-x, y-0.5, 0.5-z$ ; (viii)  $-x, y-0.5, 0.5-z$ .

evacuated silica ampoule for 3 d at 1373 K. Crystal:  $0.072 \times 0.096 \times 0.192$  mm. Precessions:  $2/m$  symmetry with systematic absences  $0k0$  for  $k$  odd,  $h0l$  for  $l$  odd. Space group  $P2_1/c$ . Enraf-Nonius CAD-4 diffractometer. Unit cell: least squares on 25 reflections,  $\pm 2\theta$ ,  $36 < 2\theta < 44^\circ$ . Intensity measurement by  $\omega$ - $\theta$  of  $(1.08 + 0.35 \tan\theta)^\circ$  and  $(1 + \tan\theta)$  mm counter aperture slit determined by a study of some reflections in the  $\omega$ - $\theta$  plane. Scanning speed adjusted to obtain  $\sigma(I)/I < 0.018$  or to approach it in a time limited to 60 s. Three standards for count every 2000 s and orientation every 600 reflections: no appreciable trends. 5587 reflections measured, 2792 reflections ( $h \pm 15, k 20, l 16, 2 < \theta < 45^\circ$ ) with  $I/\sigma(I) \geq 3$  used to solve and refine the structure. No correction made for extinction and absorption. All subsequent calculation on a MicroVAX II with the SDP system (B. A. Frenz & Associates Inc., 1982). All atoms refined anisotropically. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).  $(\Delta/\sigma)_{\max} = 0.63$ ,  $\Delta\rho < 4.62 \text{ e } \text{Å}^{-3}$ ,  $R = 0.039$ ,  $wR = 0.054$ ,  $w = 1/\sigma^2$ ,  $S = 1.897$ . Atomic parameters in Table 1.\*

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51729 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

**Discussion.** The framework of  $\text{RbMoP}_2\text{O}_7$  is similar to those observed for  $\text{KMoP}_2\text{O}_7$  and  $\text{CsMoP}_2\text{O}_7$ . It is built up from corner-sharing  $\text{MoO}_6$  octahedra and  $\text{P}_2\text{O}_7$  groups (Fig. 1).

The  $\text{Mo}^{\text{VI}}\text{O}_6$  octahedra are characterized by three short Mo—O distances and three longer ones (Table 2) as in other  $\text{Mo}^{\text{VI}}$  compounds such as  $\text{MoP}_3\text{SiO}_{11}$  (Leclaire & Raveau, 1987),  $\text{NaMoP}_2\text{O}_7$  (Leclaire *et al.*, 1988a),  $\text{CsMoP}_2\text{O}_7$  (Lii & Haushalter, 1987),  $\text{KMoP}_2\text{O}_7$  (Leclaire *et al.*, 1989), or  $\text{Mo}_4\text{P}_6\text{Si}_2\text{O}_{25}$  (Leclaire, Lamire & Raveau, 1988).

The  $\text{PO}_4$  tetrahedra present the features usually observed in the diphosphate groups: one long distance corresponding to the bridging oxygen of the  $\text{P}_2\text{O}_7$  group and three shorter bonds corresponding to the O atoms shared with the  $\text{MoO}_6$  octahedra (Table 2).

As in other alkaline molybdenum diphosphates, one observes  $\text{MoP}_2\text{O}_{11}$  units where a diphosphate group shares two of its corners with the same  $\text{MoO}_6$  octahedron. These units form layers with heptagonal windows (Fig. 1). The stacking along [001] of these layers alternately with their enantiophorph creates two

types of tunnels connecting cages where the Rb atoms are located and realize a tenfold coordination (Table 2).

#### References

- B. A. FRENZ & ASSOCIATES, INC. (1982). *SDP Structure Determination Package*. College Station, Texas, USA.
- HOK-NAM, N. G. & CALVO, C. (1973). *Can. J. Chem.* **51**, 261–262.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- LECLAIRE, A., BOREL, M. M., GRANDIN, A. & RAVEAU, B. (1988a). *J. Solid State Chem.* **76**, 131–135.
- LECLAIRE, A., BOREL, M. M., GRANDIN, A. & RAVEAU, B. (1988b). *Z. Kristallogr.* **184**, 247–255.
- LECLAIRE, A., BOREL, M. M., GRANDIN, A. & RAVEAU, B. (1989). *J. Solid State Chem.* **78**, 220–226.
- LECLAIRE, A., LAMIRE, M. & RAVEAU, B. (1988). *Acta Cryst.* **C44**, 1181–1184.
- LECLAIRE, A. & RAVEAU, B. (1987). *J. Solid State Chem.* **71**, 283–290.
- LIU, K. H. & HAUSHALTER, R. (1987). *Acta Cryst.* **C43**, 2036–2038.
- RIOU, D., LABBÉ, PH. & GOREAUD, M. (1988). *Eur. J. Solid State Inorg. Chem.* **25**, 215–229.

*Acta Cryst.* (1989). **C45**, 991–993

## Structure of $\text{Mo}_8\text{Ga}_{41}\text{S}$

BY M. WOŁCYRZ, R. ANDRUSZKIEWICZ AND K. ŁUKASZEWICZ

*Institute for Low Temperature and Structure Research, Polish Academy of Sciences, Pl. Katedralny 1, 50–950 Wrocław, Poland*

(Received 30 March 1988; accepted 3 January 1989)

**Abstract.**  $M_r = 3658.1$ , tetragonal,  $I4/m$ ,  $a = 12.861$  (3),  $c = 5.284$  (1) Å,  $V = 873.94$  Å<sup>3</sup>,  $Z = 1$ ,  $D_m = 6.96$  (1),  $D_x = 6.950$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 353.46$  cm<sup>-1</sup>,  $F(000) = 1623$ ,  $T = 298$  K,  $R = 0.045$  for 1012 unique observed [ $|F_o| > 3\sigma(F_o)$ ] reflections. The structure can be described by two types of coordination polyhedra:  $\text{MoGa}_{10}$  and  $(\text{S,Ga})\text{Ga}_{12}$ . The twofold position 0,0,0.5 is statistically occupied by S and Ga atoms.

**Introduction.** Two intermetallic phases exist in a Mo—Ga phase diagram: cubic  $\text{Mo}_3\text{Ga}$  and monoclinic  $\text{Mo}_6\text{Ga}_{31}$  (Bornand, Siemens & Oden, 1973; Wood, Compton, Matthias & Corenzwit, 1958; Matthias, Wood, Corenzwit & Bala, 1956; Yvon, 1974). Gallium-rich alloys are, however, sensitive to the introduction of small amounts of elements from the oxygen group of the periodic table and the rhombohedral phase  $\text{Mo}_8\text{Ga}_{41}$  reported by Yvon (1975) was shown by

Horyń & Andruszkiewicz (1985) to contain oxygen. The introduction of sulfur results in a new gallium-rich tetragonal phase (Andruszkiewicz & Horyń, 1988). Isomorphous phases containing selenium and tellurium have been reported by Horyń & Andruszkiewicz (1982).

This paper presents results of the structure analysis performed on a single crystal with nominal composition  $\text{Mo}_8\text{Ga}_{41}\text{S}$ .

**Experimental.** Molybdenum (purity 99.95%), gallium (99.999%) and sulfur (99.8%) taken as starting materials for single-crystal growing. A mixture of  $\text{MoS}_2$  and Mo in the proportion 1:15 was placed as a pellet in the hot end of a boat containing gallium. Crystallization occurred in an evacuated and sealed-off quartz ampoule during 5 d. Single crystals were grown in a colder area of a boat at a temperature of 973 K, separated from gallium by dissolving the excess gallium