High pressure forms of BPO₄ and BAsO₄; quartz analogues.* By Frank Dachille and L. S. Dent

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(*Received 5 May 1959 and in revised form 10 June 1959*)

The existence of phases with structures analogous to those of the silica minerals has long been known. In particular the structures of BPO_4 and $BAsO_4$ under room temperature conditions were reported by Schulze (1934) to be analogous to high cristobalite, (with B,P or B,As replacing Si,Si in an ordered way) while Machatschki (1935, 1936) and Huttenlocher (1935) studied $AlAsO_4$ and $AlPO_4$ and found these to be similarly derived from the quartz structure.

In a series of papers from this laboratory the polymorphism of these half-breed derivatives has been under re-examination. Shafer, Shafer & Roy (1956) reported that a possible BPO_4 analogue of quartz was formed under mild hydrothermal conditions, but they noted that the material was anomalously low in density for a quartz-structure polymorph. In a later investigation, Dachille & Roy (1957) were able in fact to prepare the quartz form of BPO_4 in uniaxial pressure devices at about 50,000 atmospheres and 500 °C. A p–t equilibrium curve was also presented at that time. Mackenzie, Roth & Wentorf (1959) more recently reported the formation of high pressure forms of BPO_4 and $BAsO_4$. They stated that these were new forms with c/a ratios unlike both silica–C (coesite) and quartz; they indexed their powder patterns on a hexagonal unit cell (Tables 1 and 2).

A further examination of BPO_4 and $BAsO_4$ was undertaken to check whether or not the phases prepared by Mackenzie *et al.* (1959) were indeed even higher pressure forms than the BPO_4 quartz form reported by Dachille & Roy (1957). The results showed that the materials prepared by Mackenzie *et al.* (1959) were identical to the earlier materials and were in fact quartz forms, and that the unit cells assigned by them were incorrect. Details of the synthesis and equilibrium investigations are being published elsewhere.

Samples of the high pressure forms of BPO_4 and $BAsO_4$ were prepared as described earlier (Dachille & Roy, 1957) except that the latter could be prepared at pressures as low as 40,000 atmospheres. Powder patterns of the products were substantially in agreement with those very

kindly supplied by Mackenzie. (See Table 2). Small single crystals were obtained of both materials, which, especially in the BPO_4, were often perfect hexagonal prisms. The unit cells were determined directly, and were found to be analogous to that of quartz, except that the c-axis in each case is doubled (Table 1). Rotation and Weissenberg photographs about a and c showed that the crystals had trigonal symmetry, with a threefold screw axis parallel to c. This is consistent with the assumption that they are derived from the quartz structure in the same way as the earlier studied $AlPO_4$ and $AlAsO_4$. The odd layers present in the c-rotation photographs (which correspond to the doubling of c) are connected with the ordering. If these layers are ignored, comparison with c-rotation photographs of quartz shows that the intensity distributions are very similar. This leaves little doubt that the structures are closely related to that of quartz in the way suggested, and comparison of calculated and observed intensities for the 00·l and h0·0 reflections of BPO_4 (making suitable adjustments of interatomic distances) confirmed this.

The cell derived by Mackenzie *et al.* (1959) is related to the true cell, their c being correct and their a corresponding to the long diagonal of the base of the true cell (Table 1). In view of this, it is hardly surprising that they found that c/a was appreciably different from that of quartz. Table 1 shows this ratio for the true cell, compared to that for quartz with c doubled; this last is necessary to make the comparison meaningful, since the cells compared should have an equal number of oxygen atoms.

The powder patterns are quoted in Table 2. They are almost identical with those quoted by Mackenzie *et al.* (1959), the only significant difference being that two very, very weak lines reported by Mackenzie *et al.* (1959) in the BPO_4 pattern, and indexed by them as 20·0 and 20·1, were not detected in the present work. The present patterns were indexed by direct comparison of single crystal and powder photographs taken on the same 6 cm. diameter camera; indices and calculated spacings are given in Table 2. This is the easiest and most fool-proof method of indexing powder patterns, since it enables lines caused by β-radiation or by extraneous phases to be distin-

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* Contribution No. 58–86.

Table 1. *Unit cells, densities, and refractive indices*

SiO₂ Quartz*	BPO₄		BAsO₄	
	Mackenzie *et al.*	Present work	Mackenzie *et al.*	Present work
a 4·913	$7·75 \pm 0·02 (4·47 \times \sqrt{3})$	$4·470 \pm 0·005$	$7·91 \pm 0·02 (4·567 \times \sqrt{3})$	$4·562 \pm 0·005$
c 5·405	$9·95 \pm 0·02$	$9·926 \pm 0·01$	$10·32 \pm 0·02$	$10·33 \pm 0·01$
c/a 2·20†	1·28	2·22	1·31	2·26
Z3(SiO₂)		3(BPO₄)		3(BAsO₄)
ϱ (X-ray) 2·647	3·05	3·069	3·98	4·00₄
ϱ (obs.)	$3·05 \pm 0·05$	$3·05 \pm 0·02$	$3·9 \pm 0·2$	Not determined
ω 1·544	$1·636 \pm 0·002$	$1·639 \pm 0·002$	$1·740 \pm 0·002$	$1·730 \pm 0·002$
ε 1·553	$1·648 \pm 0·002$	$1·647 \pm 0·002$	$1·748 \pm 0·002$	$1·757 \pm 0·002$

* Quartz values from Swanson and Fuyat, N.B.S. Circular 539, Vol. III (1953).
  Card No. 5–0490 in the X-ray Powder Data File.
† Referred to cell with c doubled.

Table 2. *Powder data for* BPO$_4$ *and* BAsO$_4$ *(Quartz forms)*

| | BPO$_4$ | | | | | BAsO$_4$ | | | | |
| | Mackenzie *et al.* | | Present work | | | Mackenzie *et al.* | | Present work | | |
Index	d_O	I	d_O	I	d_c	d_O	I	d_O	I	d_c
10·0	3·895 Å	s	3·878 Å	50	3·871 Å	3·964 Å	m	3·960 Å	25	3·951 Å
10·1	3·626	m	*		3·607	3·699	s	3·694	55	3·690
	3·363	vvw								
00·3	3·318	w	*		3·309	3·452	w	3·440	40	3·443
	3·204	vvw								
10·2	3·060	vs	3·051	100	3·052	3·145	vs	3·143	100	3·138
10·3	2·519	vvw	2·515	5	2·515	2·598	vw	2·600	5	2·596
11·0	2·239	m	2·244	30	2·235	2·281	w	2·281	20	2·281
11·1	2·183	vw	2·180	7	2·181	2·228	w	2·228	10	2·227
10·4	2·092	m	2·088	15	2·089	2·162	m	2·161	20	2·162
11·2	2·040	w	2·037	15	2·038	2·087	vw	2·088	10	2·087
20·0	1·936	vvw	1·938	10	1·935	1·976	w	1·975	20	1·975
20·1						1·941	vvw	1·941	3	1·940
11·3	1·852	vvw			1·852	1·901	vw	1·903	7	1·902
20·2	1·805	vw	1·800$_5$	20	1·803					
10·5	1·768	vvw	1·764	10	1·766	1·831	w	1·831	8	1·831
00·6								1·722	13	1·722
20·3	1·671	w			1·671			1·713	20	1·713
11·4	1·662	m	1·659$_3$	30	1·661	1·710	m	1·710	25	1·710
10·6								1·578	8	1·579
20·4	1·527	w	1·526$_6$	10	1·526	1·568	vw	1·570	5	1·569
11·5	1·485	vvw			1·484	1·530	vw	1·530	5	1·531
21·1	1·448	vw			1·447	1·476	vw	1·477	13	1·478
21·2	1·403	w	1·402$_4$	50	1·403	1·433	w	1·434	15	1·434

* Obscured in our patterns by presence of some cristobalite form, which gives peaks in this region.

guished. The two extra lines included by Mackenzie *et al.* (1959) appear to be due to such causes; their inclusion necessitated the adoption of the larger unit cell by Mackenzie *et al.* (1959), and obscured the relationship to quartz.

Refractive indices and density have also been determined directly. Except for the indices of BAsO$_4$ they differ only slightly from those obtained by Mackenzie *et al.* (1959), and very kindly communicated to us personally. Both sets of results are given in Table 1.

The study of the silica phases conducted in this laboratory has been supported by the Chemical Physics branch of the U.S. Army Signal Corps over a period of years. Experimentation at high pressures is done under contract to the Office of Naval Research, Contract

N(onr) 656 (20). We are indebted to Prof. Rustum Roy for reading the manuscript.

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Unit cell and space group of uranyl acetate dihydrate, UO$_2$(CH$_3$COO)$_2$.2H$_2$O.

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Uranyl acetate dihydrate crystallises as plates and prisms from dilute acetic acid, and belongs to the orthorhombic system. The exposed crystals loose their transparency and become amorphous in one or two days. Its crystal structure has not been reported.

Rotation and Weissenberg layer photographs with Cu $K\alpha$ radiation are taken about the b and the c axes. The cell dimensions thus obtained were checked by

indexing the powder pattern obtained with a Philips counter diffractometer. The lattice parameters are

$$a = 14·95, \quad b = 9·61, \quad c = 6·93 \text{ Å}.$$

The ratio $a : 2b : c = 0·78 : 1 : 0·36$ agrees with the Groth's value $a : b : c = 0·7817 : 1 : 0·3550$ indicating that the true b-axis is half the morphological b-axis. Taking the den-