High pressure forms of BPO$_4$ and BAsO$_4$; quartz analogues.*

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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

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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-

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

SiO$_2$ Quartz*	BPO$_4$		BAsO$_4$	
	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
$Z3(SiO_2)$		$3(BPO_4)$		$3(BAsO_4)$
ϱ (X-ray)				
2·647	3·05	3·069	3·98	4·00$_4$
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.