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New high pressure modifications of BPO_4 and $BAsO_4$.

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In a recent study of phase transformations in various silica isomorphs, Dachille & Roy (1957) found that at pressures and temperatures up to 35,000 atmospheres and 550 °C., only BeF_2 yielded a dense structure corresponding to coesite–SiO_2. The compounds BPO_4 and $BAsO_4$, analogous to silica as $SiSiO_4$, are known only in the high-cristobalite modification (Schulze, 1934), a reported quartz form of BPO_4 being still unconfirmed (Shafer *et al.*, 1956). As comparatively higher pressures and temperatures are now available for phase transformation studies, the preparation of the denser polymorphs of these oxides has been reattempted. This note describes the formation of new dense modifications of BPO_4 and $BAsO_4$.

BPO_4 was obtained from Victor Chemical Works and $BAsO_4$ prepared from aqueous solutions of H_3BO_3 and As_2O_5. Chemical analysis showed the purity of the two oxides to be $> 99{\cdot}5\%$ and spectroscopic analysis revealed the absence of heavy metals. The polycrystalline samples were contained in graphite capsules and subjected to pressures of 85,000 atmospheres at 1000–1200 °C. for about 10 min. The compressed materials were crystalline and optically uniaxial. Repeated attempts have failed to produce single crystals of dimensions $> 30\ \mu$. Marked increases over the starting materials in density, by sink-float method, and refractive indices, by optical immersion, were found (Table 1). No transformations were observed by heating the dense oxides in air at 100 °C. for 24 hours. The X-ray powder diffraction data for both compounds, obtained from Debye–Scherrer and spectrometer methods, are similar and can be indexed on the basis of a hexagonal unit cell, the dimensions of which are presented in Table 1. The spectrometer data are given in Table 2. The c_0/a_0 ratios are appreciably different from those of α-quartz (1·10) and coesite (1·73). However, allowing for the differences between the Si–O and B–O, P–O, and As–O bond lengths, the volumes of individual BPO_4 and $BAsO_4$ groups are approximately equal to that of 2 SiO_2 in α-quartz.

Table 1. *Unit-cell dimensions, density and refractive indices of dense* BPO_4 *and* $BAsO_4$

	BPO_4	$BAsO_4$
a_0 (Å)	7·75 ±0·02	7·91 ±0·02
c_0 (Å)	9·95 ±0·02	10·32 ±0·02
c_0/a_0	1·29	1·31
N (molecules/unit cell)	9	9
$\varrho_{\text{X-ray}}$ (g.cm.$^{-3}$)	3·05	3·98
$\varrho_{\text{obs.}}$ (g.cm.$^{-3}$)	3·05 ±0·05	3·9 ±0·2
ω	1·636±0·002	1·740±0·002
ε	1·648±0·002	1·748±0·002

Table 2. *X-ray powder diffraction data for dense* BPO_4 *and* $BAsO_4$

(Co $K\alpha$, $\lambda = 1{\cdot}5405$ Å)

BPO_4		$BAsO_4$		
d_0 (Å)	*I*	d_0 (Å)	*I*	*hkl*
3·895	*s*	3·964	*m*	110
3·626	*m*	3·699	*s*	111
3·363	*vvw*			200
3·318	*w*	3·452	*w*	003
3·204	*vvw*			201
3·060	*vs*	3·145	*vs*	112
2·519	*vvw*	2·598	*vw*	113
2·239	*m*	2·281	*w*	300
2·183	*vw*	2·228	*w*	301
2·092	*m*	2·162	*m*	114
2·040	*w*	2·087	*vw*	302
1·936	*vvw*	1·976	*w*	220
		1·941	*vvw*	221
1·852	*vvw*	1·901	*vw*	303
1·805	*vw*			222
1·768	*vvw*	1·831	*w*	115
1·671	*w*			223
1·662	*m*	1·710	*m*	304
1·527	*w*	1·568	*vw*	224
1·485	*vvw*	1·530	*vw*	305
1·448	*vw*	1·476	*vw*	411
1·403	*w*			412
		1·433	*w*	216
		1·381	*vvw*	117
1·339	*vvw*	1·357	*vvw*	413
1·333	*vvw*			306
1·280	*vvw*	1·307	*vvw*	331
1·260	*vw*	1·296	*vw*	226

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