Crystal Structures of Betaine Phosphate/Arsenate Mixed Crystal

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Single crystal of a betaine-phosphate/arsenate mixed system (30% P was replaced with As randomly) was investigated by means of X-ray diffraction. The crystal structures of room temperature and of low temperature (20 K) were determined. At room temperature, the least-squares method converged at the R factor 3.6 % with 1038 reflections. The structure is isomorphous to pure betaine phosphate. For the low-temperature structure the R factor converged at 4.3 % with 4896 reflections (3.7 % with 2987 normal reflections and 9.6 % with 1909 superlattice reflections). The structure analysis clarifies that the hydrogen atoms of the phosphoric acid between neighboring phosphate tetrahedra are ordered in the low temperature phase resulting the superstructure (the unit cell dimension along the a-axis is doubled). By replacing P with As up to 30 % in $P(As)O_4$ tetrahedra, the unit cell structure is changed little; only the mean size of the tetrahedra is enlarged by 2.2 %.

§1. Introduction

More than a decade ago, a mixed crystal system of betaine phosphate[1] and betaine arsenate[2] was interested as a candidate of dipole glass.[3] Pure betaine arsenate $(CH_3)_3NCH_2COO \cdot H_3AsO_4$ (abbreviated BA, hereafter) is ferroelectric below 119K,[2] while pure betaine phosphate $(CH_3)_3NCH_2COO \cdot H_3P O_4$ (abbreviated BP, hereafter) is antiferroelectric below 86K. [1] The mixed crystals display ferroelectricity and antiferroelectricity for As-rich and P-rich sides, respectively.[4] Though a rather broad anomaly was detected in dielectric constants at low temperature for the intermediate crystals of $BP_{1-x}BA_x$ with $0.5 \leq x \leq 0.85$, where x is the molar ratio of arsenate,[3] no direct evidence of dipole glass, such as the RDP-ADP mixed system, [5] was convinced yet.

A few years ago, the mixed crystals with $0.1 \leq x \leq 0.4$ were investigated again. Kim and his coworkers attributed a peculiar kink in the temperature dependence of the dielectric constant to a phenomenon of the dimensional crossover. [6] With decreasing temperature the dielectric constant firstly increased in according to the relation for the quasi-1D Ising model. Below T_d=85 K,

the dielectric constant obeyed the Curie-Weiss law (3-dimensional system) with approaching the antiferroelectric phase transition at T_a=77 K in the mixed crystals of $x = 0.4$ and 0.3.

On the other hand, it has been reported that the mixed crystal system undergoes two phase transitions at about T_3=85 and T_4=80 K, which were detected in the dielectric constant,[7] the specific heat anomaly, [8,9] the elastic constant, [10] and so on. The X-ray diffraction study indicates the unit cell dimension is doubled below 82K and 75K for x=0.2 and 0.4 systems, respectively. But no additional phase transition was found in the mixed systems around 80 K .[11]

In order to clarify the relation between the dielectric anomaly and the intermediate phase detected by specific heats and others, we have observed X- ray scattering from the mixed crystal of $x = 0.4$.[12] Superlattice reflections appeared definitely below 75K, which temperature was considered to correspond to T_4. In the intermediate temperature range between T_3 and T_4, very weak superlattice reflections could be recognized. However, the mixed crystal was damaged by X-ray irradiation because As atom absorbed X-ray heavily and the hydrogen bonding in the crystal might be affected.[12] It has not been concluded definitely whether T_3 and T_4 correspond to T_d and T_a, respectively.

By the way, betaine phosphate(BP) and betaine arsenate(BA) are not isostructural with each other. The space groups of BP are $P2_1/m$ (Z=2) in phase I above 365K, $P2_1/c$ (Z=4) in phase II between 365K and 86K, and $P2_1/c$ (Z=8) at low temperature. [13] In phase I the betaine and phosphate molecules are disordered against the mirror planes perpendicular to the b axis. The molecules are ordered alternatively in phase II to double the cell dimension along the c-axis.[13] Below 86K, the unit cell is further elongated twice along the a-axis. [11] It is found that the disordered hydrogen atoms between the phosphate tetrahedra become ordered in the low-temperature phase with accompanying small antiferroelectric displacements.[14]

Meanwhile, the space groups of BA are reported as follows: $Pcnm$, $P2_1/n$ and Pc in phase I (above 411K), phase II and ferroelectric phase III (below 119K); the formula unit is four in all phases. [2,15] Although the local configurations between betaine and arsenate are similar to those between betaine and phosphate, the unit-cell structure is a little different between BP and BA.

From the phase diagram of the system of $BP_{1-x}BA_x$, [3] it is considered that the mixed crystal systems of $x \leq 0.4$ are similar to pure BP and the ones of $0.9 \leq x$ are to pure BA. However, no structural study has been reported on the mixed system in so far as author's knowledge. In order to give the structural data of the mixed crystal system of $BP_{1-x}BA_x$, we investigate the crystal of $x = 0.3$. The specimen was cut from the same crystal that dimensional crossover has been investigated by Kim et al.[6] We determine the crystal structures of the mixed crystal at 20 K in low- temperature phase and at 298 K in room-temperature phase by X-ray diffraction, and investigate the structural change through the antiferroelectric transition. The structures will be compared with those of pure BP.

§2. Experimental

The mixed crystals of $BP_{1-x}BA_x$ were grown by the evaporation method. Small pieces of samples were cut from the transparent single crystals and were made cube in $0.5 \times 0.5 \times 0.5$ mm^3. A sample was attached to the end of a copper needle and was cooled by a closed He-gas cycle-type cryostat. The specimen was enclosed by a beryllium cover to keep the uniformity of temperature, which was kept at 20 ± 0.1 K during the intensity measurement. An off-center type four-circle diffractometer manufactured by HUBER was controlled by the MXC system (MAC SCIENCE) to collect data.

X-ray was generated from a rotating anode generator operating at 45 kV and 200 mA. Mo $K\alpha$ radiation was monochromated with the use of a pyrolytic graphite. The wavelength of the X-ray was λ=0.71074 Å. The integrated intensity was obtained by the $2\theta/\omega$ scanning mode with the scan speed of $10°$/min in the range of $2\theta < 60°$.

The AXS89 program was employed to analyze the crystal structure.[16] Atomic scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography*.[17] Although the nominal value of x, which was assumed to be the molar ratio in the aqueous solution prepared, was 0.4, a chemical analysis for As revealed that the molar ratio of the crystal was $x = 0.3$. The parameter x was assigned as 0.2 in our preliminary analysis, [12] for which the absorption correction was done with the fixed value of x. However, the linear absorption coefficient μ depended on x. We tried the structure analysis for $0.1 \leq x \leq 0.4$, and found that $x = 0.3$ gave most successful results. The crystal data are summarized in Table I.

§3. Results

3.1 The structure at 20 K

We have reported that the superlattice reflections of mixed crystal of $BP_{1-x}BA_x$ became weak by X-ray radiation damage and disappeared at last.[12] It took about a week to collect the intensity, during which only superlattice reflections became weak. To reduce the radiation damage, we measured two samples; one was measured from high angle indices and the other from the low angle ones. We applied a decay correction by using the monitor intensity of two strong superlattice reflections. The index range of the whole reflections was $-28 \leq h \leq 31$, $0 \leq k \leq 10$, $-17 \leq l \leq 16$, and the number of measured reflections was 9425.

The strong reflections with $F > 5\sigma(F)$ were selected and equivalent reflections ($F(hkl)$ and $F(\bar{h}\ k\ \bar{l})$) were averaged. Moreover, some weak reflections against the extinction rule of $h0l$: $h + l = odd$ and $0k0$: $k = odd$ were eliminated. We thought that such reflections stemmed from diffraction by the Be cell, multiple scattering in the crystal, or so on. The number of unique reflections was 4896 finally.

Firstly, the structure was analyzed about atoms of C, N, O, P and As without hydrogen. The P atom was assumed to be replaced randomly by As. The positional parameters of As were

determined with no constraint; both P and As atoms converged to almost the same positions. Secondly, a differential Fourier synthesis was applied to get the positions of H. The electron density corresponding to the hydrogen atoms H1 $\sim$ H12 and H15 $\sim$ H26 was 0.95 $\sim$ 1.28 eÅ^{-3}. The electron density corresponding to the hydrogen atoms H13, H14, H27, H28 was 0.49 $\sim$ 0.80 eÅ^{-3}. Thirdly, the least-squares calculations were performed for all atoms.

The final result of the least-squares calculations converged at R=0.0431, S=1.64, $(\Delta/\sigma)_{max} <$ 0.13 for the reflections N_o= 4896, the unique parameters N_p=376 with anisotropic thermal parameters. The R factor for 2987 normal reflections was 0.0365, and the R factor for 1909 superlattice reflections was 0.0956. The atomic coordinates and the equivalent thermal parameters are summarized in Table II. The reflection data and the anisotropic thermal parameters are deposited. [18] Figure 1 shows one of the moleculer units of the mixed crystal.

Figure 2 shows the differential Fourier map of the electron density in $0.45 \leq x \leq 0.70$, $0.10 \leq z \leq 0.60$, and y=0.24. The gray area in the figure indicates the negative density. One of the double peak (0.58, 0.23, 0.26) with the electron density 0.67 eÅ^{-3} was assigned as a part of the hydrogen atom H14. And the peak (0.53, 0.24, 0.24) with the electron density 0.49 eÅ^{-3} was the other part of the disordered hydrogen atom H14a. The single peak (0.61, 0.23, 0.48) with the electron density 0.95 eÅ^{-3} was the hydrogen atom H12. The circles in Fig. 2 show the final positions of these hydrogen atoms after the least-squares calculations.

Two hydrogen atoms which link betaine and $H_2P(As)O_4$ have split peaks in the differential Fourier maps. These atoms are assumed to occupy two positions stochastically. Their occupation probability is fitted by the calculations. The multiplicity of hydrogen H14 is obtained as H14 : H14a = 0.458(9) : 0.542, and that of H28 is as H28 : H28a = 0.594(8) : 0.406.

3.2 The structure at 298 K

The number of observed reflections within $2\theta < 60°$ was 2528 at room temperature. Strong reflections with $F > 3\sigma(F)$ were averaged for equivalent ones with $F(hkl)$ and $F(\bar{h}\,k\,\bar{l})$. After eliminating those against the reflection conditions, we used 1038 independent reflections for structural analysis, which proceeded in the same way as 20 K.

The differential Fourier maps revealed hydrogen atoms with their electron density of 0.18 $\sim$ 0.45 eÅ^{-3}. Although these peaks were rather weak in comparison to those of 20 K, the peak positions were corresponding to the hydrogen atoms at low temperature. Since the positional parameters of the disordered H14 were rather unstable, the positional parameter of H14a were fixed at those of pure BP(later given in Table VI) in the least-squares calculations. After a number of iteration, all fitting parameters were obtained. The final results are $R = 0.0359$, $S = 0.61$, $(\Delta/\sigma)_{max} < 0.057$ for independent parameters of N_p=190 (Table I). The positional parameters and the equivalent thermal parameters are given in Table III.

The multiplicity of disordered hydrogen H14 was estimated as H14 : H14a = 0.63(6) : 0.37. On

the other hand, both H13 and H13a have their counter parts by symmetry, and their multiplicity is 0.5.

§4. Discussions

The interatomic distances in the low-temperature phase are summarized in Table IV. The bond length of P-O and As-O in $P(As)O_4$ is 1.577 Å on the average; it is 2.2 % longer than that of BP.[14] The interatomic distances between two oxygen atoms connected by hydrogen bonding, $O1 \cdots H12-O3$, $O2-H14a(H14) \cdots O6$, $O7 \cdots H26-O9$ and $O8-H28(H28a) \cdots O12$, are $2.45 \sim 2.62$ Å. The inetratomic distances between the neighboring phosphate tetrahedra, $O4 \cdots H27(i)-O10(i)$ and $O5-H13 \cdots O11(ii)$, are $2.49 \sim 2.51$ Å. Here the numbers indicate the symmetry code (i) $(1-x, -y, 1-z)$ and (ii) $(1-x, 1-y, 1-z)$.

At 20K, the similarity of structure is also confirmed between the mixed crystal given in Table II and BP given in Table II of reference 14. The centers of mass of the PO_4 tetrahedra and the betaine molecules sit at positions within 0.02 Å between the mixed crystal and BP. The tilt angles of the molecules plane about a axis of (0.57, -0.58, 0.58) coincide are within $\pm 0.405°$. Therefore the structural change of the mixed crystal between room temperature and 20K quite resembles to that of BP.

At room temperature, the interatomic distances are given in Table V. The mean distance between P(As) and O is 1.567 Å; it is 1 % shorter than that of 20 K because no correction for thermal vibration is made. The interatomic distances between oxygen atoms are $2.47 \sim 2.48$ Å, as same as 20K. The projection along the a-axis is plotted in Fig. 3.

In order to compare the structure of the mixed crystal with BP, we refined the room temperature structure of BP, for which the atomic parameters has not been given explicitly; only those for deuterated crystal of BP were published. [13] The result is in agreement with ref. 13, and is given in Table VI. The positional parameters almost coincide with Table III. The centers of mass of $P(As)O_4$ tetrahedron and the betaine molecule shift within ± 0.02 Å between the mixed crystal and BP. The tilt angles of the molecules about a axis of (0.37, -0.66, 0.66) coincide within $\pm 0.455°$.

In the low-temperature structure, betaine molecules and $P(As)O_4$ tetrahedra translate slightly from the room-temperature positions. The molecules also tilt against the a-c plane; the tilting angles change. The tetrahedron which contains P1 rotates about an axis of (-0.97, 0.17, -0.17) by 1.3°, while that contains P2 rotates about (0.97, -0.17, 0.17) by -1.3°. This means the counterpart rotation takes place about the antiparallel axes. The mass centers of oxygen atoms of tetrahedra are (0.6786, 0.2526, 0.4122) and (0.1792, 0.2544, 0.4154). These positions differ slightly from P1 or As1 and P2 or As2. That is, the P and As atoms deviate from the center of the oxygen tetrahedra by -0.018 Å for P1 and +0.036 Å for P2 along the b axis. The translation along the a axis and c axis are small. These derivations are similar in the pure BP crystal at 20 K; -0.022 Å for P1 and +0.037 Å for P2. Such deviations also contribute to the antiferroelectric dipole alignment of the

distorted PO_4 tetrahedra.

Finally the most drastic difference between room-temperature and 20 K structures is the ordering of hydrogen atoms. At room temperature, H13 and H13a occupy two equivalent positions with probability of one half (see Fig. 3 and Fig.4 of ref. 14). In low temperature, H13 takes the position near-by O5, while H27(H13a) near-by O10. The ordering of these hydrogen atoms accompanies the antiferroelectric displacement of the betaine and phosphate molecules, though the amount is at most 0.02Å, just as in the case of pure BP.[14] It is convincing that the mixed system of $BP_{1-x}BA_x$ ($x \leq 0.3$) performs the similar phase transitions as pure BP from the structural points.

In summary we have determined the mixed crystal structures of $BP_{1-x}BA_x$ ($x = 0.3$). Both at room temperature and at 20 K, the structures coincide to those of pure BP. Therefore the peculiar behavior of the dielectric constant in the mixed system cannot be explained from a structural viewpoint. It has been reported that the dielectric constant shows an abnormal enhancement under the electric bias field.[7] The mixed crystal may have internal bias field which may affect the dielectric susceptibility. This point cannot be clarified by our structural analysis.

Acknowledgements

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Fig. 1.   One of the moleculer units at 20 K of $BP_{1-x}BA_x$ ($x = 0.3$). Atoms which belong to N1 and P1 are plotted.

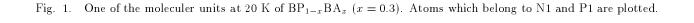Fig. 2.   The differential Fourier map of the electron density at 20K of $BP_{1-x}BA_x$ ($x = 0.3$). The circle shows coordinates of atoms as a result of structural analysis. The gray area shows the region of negative density.

Fig. 3.   Projection from the a axis at room temperature of $BP_{1-x}BA_x$ ($x = 0.3$). The half of molecules are plotted. The named betaine has a symmetry code of 1-x, 1/2+y, 1/2-z.

Table I. Crystal data of $(CH_3)_3NCH_2COO \cdot H_3P_{1-x}As_xO_4$ $(x = 0.3)$.

Data set	Room temperature	Low temperature
Space group	$P2_1/c$	$P2_1/c$
Formula unit Z	4	8
Temperature [K]	298	20
a [Å]	11.103(12)	22.223(6)
b [Å]	7.869(4)	7.824(3)
c [Å]	12.934(22)	12.682(3)
β[deg]	119.88 (9)	119.83(2)
Volume [Å^3]	983(2)	1913(1)
μ [mm^{-1}]	12.735	13.825
Index range	$-14 \leq h \leq 14$	$-28 \leq h \leq 31$
	$0 \leq k \leq 9$	$0 \leq k \leq 10$
	$-10 \leq l \leq 10$	$-17 \leq l \leq 16$
Measured reflection	2528	9425
Unique reflection	1038	4896
No.of parameters	190	376
R	0.0359	0.0431
S	0.611	1.64
$\Delta\rho$ [eÅ^{-3}]	$-0.27 < \Delta\rho < 0.18$	$-0.83 < \Delta\rho < 0.81$

Table II.   Atomic coordinates and equivalent thermal parameters of $BP_{1-x}BA_x$ ($x = 0.3$) at 20K.

	x	y	z	B_{eq}		x	y	z	B_{eq}
As1	0.67946 (4)	0.2519 (1)	0.41484 (7)	0.89 (2)	H2	0.278 (2)	0.302 (5)	0.305 (3)	0.64 (5)
As2	0.17729 (4)	0.25537 (9)	0.41336 (7)	0.94 (2)	H3	0.288 (2)	0.405 (5)	0.217 (3)	0.62 (5)
P1	0.67998 (4)	0.2486 (1)	0.40865 (7)	0.88 (2)	H4	0.363 (2)	0.101 (5)	0.445 (3)	0.62 (5)
P2	0.17850 (4)	0.2628 (1)	0.41056 (7)	0.84 (2)	H5	0.370 (2)	0.023 (5)	0.342 (3)	0.64 (5)
O1	0.52050 (8)	0.2412 (2)	0.4148 (1)	1.00 (3)	H6	0.436 (2)	0.094 (5)	0.451 (3)	0.70 (5)
O2	0.49784 (8)	0.2615 (2)	0.2216 (1)	1.13 (4)	H7	0.379 (2)	0.411 (5)	0.475 (3)	0.56 (5)
O3	0.65346 (8)	0.2194 (2)	0.5070 (1)	1.00 (3)	H8	0.396 (2)	0.517 (5)	0.391 (3)	0.70 (5)
O4	0.74523 (8)	0.1401 (2)	0.4503 (1)	0.93 (3)	H9	0.451 (2)	0.387 (5)	0.480 (3)	0.56 (5)
O5	0.69605 (8)	0.4463 (2)	0.4103 (2)	1.04 (4)	H10	0.382 (2)	0.191 (5)	0.194 (3)	0.33 (4)
O6	0.61953 (8)	0.2045 (2)	0.2812 (1)	1.00 (3)	H11	0.390 (2)	0.386 (5)	0.211 (3)	0.53 (5)
O7	0. 1983 (8)	0.2340 (2)	0.4146 (1)	1.01 (3)	H12	0.622 (2)	0.222 (6)	0.489 (3)	0.78 (5)
O8	0.99728 (8)	0.2492 (2)	0.2210 (1)	1.16 (4)	H15	0.776 (2)	0.203 (5)	0.202 (3)	0.67 (5)
O9	0.15435 (8)	0.2298 (2)	0.5113 (1)	0.96 (3)	H16	0.777 (2)	0.291 (5)	0.300 (3)	0.61 (5)
O10	0.24578 (8)	0.1472 (2)	0.4561 (1)	0.98 (3)	H17	0.787 (2)	0.397 (5)	0.219 (3)	0.72 (5)
O11	0.19721 (8)	0.4475 (2)	0.4075 (2)	1.03 (4)	H18	0.863 (2)	0.096 (5)	0.443 (3)	0.60 (5)
O12	0.11944 (8)	0.1930 (2)	0.2865 (1)	0.96 (3)	H19	0.870 (2)	0.013 (5)	0.344 (3)	0.59 (5)
N1	0.37488 (9)	0.2721 (2)	0.3365 (2)	0.74 (4)	H20	0.934 (2)	0.089 (5)	0.449 (3)	0.70 (5)
N2	0.87369 (9)	0.2671 (2)	0.3342 (2)	0.75 (4)	H21	0.879 (2)	0.405 (5)	0.474 (3)	0.47 (5)
C1	0.2976 (1)	0.2980 (3)	0.2607 (2)	1.05 (5)	H22	0.897 (2)	0.509 (5)	0.390 (3)	0.73 (5)
C2	0.3879 (1)	0.1010 (3)	0.3982 (2)	0.99 (5)	H23	0.946 (2)	0.380 (5)	0.476 (3)	0.52 (5)
C3	0.4042 (1)	0.4123 (3)	0.4306 (2)	1.01 (5)	H24	0.881 (2)	0.189 (5)	0.193 (3)	0.35 (4)
C4	0.4029 (1)	0.2792 (3)	0.2500 (2)	0.83 (4)	H25	0.891 (2)	0.374 (5)	0.210 (3)	0.45 (5)
C5	0.4812 (1)	0.2579 (3)	0.3039 (2)	0.86 (4)	H26	0.120 (2)	0.229 (5)	0.492 (3)	0.71 (5)
C6	0.7966 (1)	0.2929 (3)	0.2575 (2)	1.05 (5)	H13	0.720 (2)	0.470 (5)	0.447 (3)	0.74 (5)
C7	0.8862 (1)	0.0963 (3)	0.3965 (2)	1.03 (5)	H14	0.588 (4)	0.219 (11)	0.262 (7)	0.41 (10)
C8	0.9026 (1)	0.4078 (3)	0.4275 (2)	0.99 (5)	H14a	0.521 (3)	0.255 (9)	0.241 (6)	0.68 (9)
C9	0.9024 (1)	0.2719 (3)	0.2490 (2)	0.82 (4)	H27	0.251 (2)	0.109 (5)	0.472 (3)	0.65 (5)
C10	0.9803 (1)	0.2491 (3)	0.3037 (2)	0.86 (4)	H28	0.019 (3)	0.238 (9)	0.241 (6)	0.70 (8)
H1	0.278 (2)	0.211 (5)	0.209 (3)	0.75 (5)	H28a	0.090 (4)	0.205 (13)	0.268 (8)	0.40 (11)

Table III. Atomic coordinates and equivalent thermal parameters of $BP_{1-x}BA_x$ ($x = 0.3$) at room temperature.

	x	y	z	B_{eq}
As	0.35889 (6)	0.25330 (8)	0.41308 (9)	1.72 (2)
P	0.3556 (2)	0.2538 (3)	0.4143 (3)	8.35 (11)
O1	0.0395 (2)	0.2412 (3)	0.4134 (3)	5.11 (11)
O2	0.9948 (2)	0.2515 (4)	0.2249 (3)	5.77 (12)
O3	0.3050 (2)	0.2258 (3)	0.5070 (3)	4.50 (10)
O4	0.4897 (2)	0.1415 (3)	0.4551 (3)	4.60 (10)
O5	0.3962 (2)	0.4414 (2)	0.4126 (3)	4.81 (10)
O6	0.2415 (2)	0.2013 (3)	0.2861 (3)	4.93 (11)
N	0.7489 (2)	0.2643 (3)	0.3347 (3)	3.23 (9)
C1	0.5937 (3)	0.2848 (5)	0.2579 (5)	5.18 (16)
C2	0.7774 (3)	0.0973 (4)	0.3985 (4)	4.91 (15)
C3	0.8042 (4)	0.4040 (4)	0.4266 (5)	4.97 (16)
C4	0.8051 (3)	0.2711 (4)	0.2516 (4)	3.68 (12)
C5	0.9618 (3)	0.2522 (4)	0.3041 (4)	3.60 (12)
H1	0.542 (4)	0.192 (5)	0.192 (6)	6.4 (13)
H2	0.561 (3)	0.278 (4)	0.314 (5)	3.6 (9)
H3	0.571 (4)	0.385 (5)	0.218 (5)	5.1 (11)
H4	0.726 (3)	0.099 (4)	0.437 (4)	2.7 (8)
H5	0.736 (3)	0.014 (4)	0.336 (4)	3.2 (8)
H6	0.882 (3)	0.097 (4)	0.459 (4)	3.0 (8)
H7	0.755 (4)	0.394 (5)	0.477 (5)	4.6 (10)
H8	0.778 (4)	0.495 (5)	0.379 (5)	4.8 (10)
H9	0.911 (3)	0.374 (4)	0.482 (5)	3.6 (9)
H10	0.764 (3)	0.185 (4)	0.195 (4)	2.6 (8)
H11	0.779 (3)	0.375 (4)	0.207 (4)	2.3 (7)
H12	0.229 (4)	0.228 (5)	0.493 (6)	6.3 (12)
H13	0.460 (5)	0.479 (7)	0.470 (7)	1.2 (13)
H13a	0.487 (6)	0.055 (6)	0.488 (7)	1.4 (14)
H14	0.172 (5)	0.224 (6)	0.278 (7)	3.6 (14)
H14a	0.105	0.253	0.245	4.9 (28)

Table IV. Interatomic distances[Å] and angles[°] of of $BP_{1-x}BA_x$ ($x = 0.3$) at 20K. Here [*] means the averaged distance between C and the bonded H, or the averaged angle.

Atoms	Distance	Atoms	Distance	Atoms	Distance	Atoms	Distance
As1-O3	1.566 (2)	C1 -H [*]	0.91 (4)	As2-O9	1.577 (2)	C6 -H [*]	0.91 (4)
As1-O4	1.567 (2)	C2 -H [*]	0.93 (4)	As2-O10	1.584 (2)	C7 -H [*]	0.93 (4)
As1-O5	1.576 (2)	C3 -H [*]	0.95 (4)	As2-O11	1.583 (2)	C8 -H [*]	0.92 (5)
As1-O6	1.596 (2)	C4 -H [*]	0.94 (4)	As2-O12	1.559 (2)	C9 -H [*]	0.91 (4)
P1 -O3	1.644 (2)	O2 -O6	2.460 (3)	P2 -O9	1.639 (2)	O7 -O9	2.617 (3)
P1 -O4	1.531 (2)	O1 -O3	2.586 (3)	P2 -O10	1.591 (2)	O8 -O12	2.452 (3)
P1 -O5	1.589 (2)	O1 -H12	1.96 (4)	P2 -O11	1.513 (2)	O7 -H26	1.93 (4)
P1 -O6	1.544 (2)	O3 -H12	0.63 (4)	P2 -O12	1.565 (2)	O9 -H26	0.68 (4)
C5 -O1	1.243 (2)	O5 -H13	0.54 (3)	C10-O7	1.242 (2)	O10-H27	0.35 (4)
C5 -O2	1.274 (4)	O2 -H14	1.84 (9)	C10-O8	1.284 (4)	O8 -H28	0.42 (6)
C5 -C4	1.529 (3)	O6 -H14	0.62 (8)	C10-C9	1.522 (3)	O12-H28	2.05 (7)
N1 -C1	1.507 (3)	O2 -H14a	0.45 (7)	N2 -C6	1.506 (3)	O8 -H28a	1.86 (9)
N1 -C2	1.508 (3)	O6 -H14a	2.02 (8)	N2 -C7	1.511 (3)	O12-H28a	0.59 (9)
N1 -C3	1.513 (3)	O4 -O10(i)	2.51 (2)	N2 -C8	1.510 (3)	O5 -O11(ii)	2.494 (2)
N1 -C4	1.512 (4)	H14-H14a	1.41 (12)	N2 -C9	1.507 (4)	H28-H28a	1.46 (12)

Atoms	Angle	Atoms	Angle
O -As1 -O [*]	109.5 (2)	O - As2 - O [*]	109.5 (2)
O -P1 -O [*]	109.4 (2)	O - P2 - O [*]	109.4 (2)
O -C5 -C(O)[*]	120.0 (4)	O - C10 - C [*]	120.0 (4)
C -N1 -C [*]	109.4 (3)	C - N2 - C [*]	109.4 (3)
C5-C4 -N1	117.3 (4)	C10 - C9 - N2	117.4 (4)
O1-H12 -O3	173 (22)	O7 - H26 - O9	172 (20)
O6-H14 -O2	175 (37)	O8 - H28 - O12	163 (28)
O6-H14a-O2	164 (31)	O8 - H28a- O12	175 (41)
O5-H13 -O11(ii)	172 (20)	O4 - H27(i)-O10(i)	164 (24)

Table V. Interatomic distances and bond angles of $BP_{1-x}BA_x$ $(x = 0.3)$ at room temperature. Here [*] means the averaged distance between C and the bonded H, or the averaged angle.

Atoms	Distance[Å]	Atoms	Distance[Å]
As - O3	1.614 (4)	C3 - H [*]	1.00 (5)
As - O4	1.548 (3)	C4 - H [*]	0.95 (4)
As - O5	1.542 (2)	O2 - O6	2.475 (5)
As - O6	1.559 (4)	O1 - O3	2.572 (5)
P - O3	1.573 (6)	O1 - H12	1.83 (4)
P - O4	1.580 (3)	O3 - H12	0.77 (5)
P - O5	1.551 (3)	O5 - H13	0.78 (5)
P - O6	1.559 (5)	O4 - H13a	0.81 (6)
C5 - O1	1.239 (6)	O2 - H14	1.74 (6)
C5 - O2	1.248 (7)	O6 - H14	0.75 (7)
C5 - C4	1.527 (5)	O2 - H14a	1.12
N - C1	1.509 (4)	O6 - H14a	1.39
N - C2	1.503 (5)	H14 - H14a	0.69 (5)
N - C3	1.510 (5)	O5 - O5(ii)	2.468 (5)
N - C4	1.489 (7)	H13 - H13(ii)	0.91 (7)
C1 - H [*]	0.97 (5)	O4 - O4(i)	2.476 (4)
C2 - H [*]	0.98 (4)	H13a- H13a(i)	0.93 (7)

Atoms	Angle[deg]	Atoms	Angle[deg]
O -As-O [*]	109.5 (4)	C5-O1 -O3	121.7 (6)
O -P -O [*]	109.5 (5)	O1-H12 -O3	163 (17)
C4-C5-O [*]	120.0 (8)	O6-H14 -O2	165 (22)
C -N -C [*]	109.4 (6)	O6-H14a-O2	160
C5-C4-N	118.0 (7)	O4-H13a-O4(i)	165 (20)
C5-O2-O6	117.9 (6)	O5-H13 -O5(ii)	175 (26)

Table VI. Atomic coordinates and equivalent thermal parameters of BP at room temperature; $P2_1/c, Z = 4$, $a = 11.059(2), b = 7.842(1), c = 12.932(3), \beta = 119.61(1)^\circ$. The least-squared calculation converged at R=0.0421, S=0.906, $(\Delta/\sigma)_{\max} = 0.15$ for 1415 independent reflections within $2\theta < 60^\circ$. The multiplicity of atom is the following: a(H13)=a(H13a)=1/2, and a(H14)=1-a(H14a)=0.59(1).

	x	y	z	B_{eq}
P	0.3599(1)	0.2529(1)	0.4141(1)	2.54(2)
O1	0.0402(3)	0.2409(5)	0.4127(3)	4.40(11)
O2	0.9978(3)	0.2508(5)	0.2245(4)	4.98(12)
O3	0.3059(2)	0.2262(4)	0.5035(3)	3.70(10)
O4	0.4889(3)	0.1434(3)	0.4547(3)	3.75(10)
O5	0.3969(3)	0.4389(3)	0.4125(3)	4.11(10)
O6	0.2451(3)	0.2023(4)	0.2892(3)	3.89(10)
N	0.7484(3)	0.2639(4)	0.3322(3)	2.62(9)
C1	0.5920(4)	0.2848(6)	0.2567(5)	4.24(16)
C2	0.7743(5)	0.0946(5)	0.3949(5)	4.11(15)
C3	0.8021(5)	0.4052(5)	0.4235(5)	4.14(16)
C4	0.8044(3)	0.2699(5)	0.2495(4)	2.92(11)
C5	0.9615(3)	0.2516(5)	0.3026(4)	3.04(11)
H1	0.557(4)	0.183(6)	0.203(6)	3.5(2)
H2	0.545(5)	0.289(6)	0.323(6)	3.4(2)
H3	0.576(4)	0.389(5)	0.218(5)	2.4(1)
H4	0.718(4)	0.097(5)	0.449(5)	2.0(1)
H5	0.748(5)	0.005(7)	0.341(6)	4.4(2)
H6	0.878(4)	0.094(5)	0.444(5)	1.8(1)
H7	0.737(4)	0.403(6)	0.473(6)	3.6(2)
H8	0.785(4)	0.505(5)	0.375(5)	2.9(1)
H9	0.910(5)	0.382(7)	0.464(6)	4.3(2)
H10	0.761(4)	0.178(5)	0.186(5)	2.2(1)
H11	0.776(4)	0.376(6)	0.201(5)	2.7(1)
H12	0.223(4)	0.235(5)	0.486(5)	1.6(1)
H13	0.473(8)	0.473(11)	0.459(9)	1.6(2)
H13a	0.493(8)	0.057(9)	0.476(9)	1.4(2)
H14	0.174(7)	0.219(9)	0.279(8)	2.0(2)
H14a	0.105(9)	0.253(13)	0.245(12)	1.9(3)

Fig. 1.

Fig. 2.

O3

O4   P/As   O5

O6

O2

C4   C1

C5   N

C3   C2

O1

C·cos β

a   b

Fig. 3.