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Journal of Solid State Chemistry 173 (2003) 449–455

JOURNAL OF
SOLID STATE
CHEMISTRY

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High-pressure synthesis and structural characterization of three new polyphosphides, α-SrP_3, BaP_8, and LaP_5

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Received 22 November 2002; received in revised form 6 March 2003; accepted 7 March 2003

Abstract

Three novel metal polyphosphides, α-SrP_3, BaP_8, and LaP_5, were prepared in BN crucibles by the reaction of the respective stoichiometric mixtures under a high pressure of 3 GPa at 950–1000°C. Their crystal structures were determined from single-crystal X-ray data (α-SrP_3: space group $C2/m$, $a = 9.199(6)$ Å, $b = 7.288(3)$ Å, $c = 5.690(3)$ Å, $\beta = 113.45(4)°$, $Z = 4$, $R_1/wR_2 = 0.0684/0.1180$ for 471 observed reflections and 22 variables; BaP_8: space group $P{-}1$, $a = 6.762(2)$ Å, $b = 7.233(2)$ Å, $c = 8.567(2)$ Å, $\alpha = 86.32(2)°$, $\beta = 84.31(2)°$, $\gamma = 70.40(2)°$, $Z = 2$, $R_1/wR_2 = 0.0476/0.1255$ for 2702 observed reflections and 82 variables; LaP_5: space group $P2_1/m$, $a = 4.885(1)$ Å, $b = 9.673(3)$ Å, $c = 5.577(2)$ Å, $\beta = 105.32(2)°$, $Z = 2$, $R_1/wR_2 = 0.0391/0.1034$ for 1272 observed reflections and 31 variables). α-SrP_3 is isostructural with $SrAs_3$ and the crystal structure consists of two-dimensional puckered polyanionic layers $^2_\infty[P_3]^{2-}$ that stack along the c-axis yielding channels occupied by Sr^{2+} counterions. BaP_8 crystallizes in a new structure type which contains a three-dimensional infinite polyanionic framework $^3_\infty[P_3]^{2-}$, with large channels hosting the barium cations. LaP_5 is a layered compound containing $^2_\infty[P_5]^{3-}$ polyanionic layers separated by La^{3+} ions. All three compounds exhibit expected diamagnetic behaviors.

Keywords: Polyphosphides; High-pressure synthesis; SrP_3; BaP_8; LaP_5

1. Introduction

Binary metal polyphosphides are of considerable interest because these compounds show a great variety of physical properties ranging from semimetallic to semiconducting behaviors [1] and in addition, they contain polyanions with homonuclear connected phosphorus atoms which are linked in different ways to form chains of various lengths, cyclic and polycyclic systems, and one-, two- and three-dimensional infinite polymers [2]. For example, BaP_3 displays one-dimensional (1D) infinite chains $^1_\infty[P_3]^{2-}$ of linear condensed six-membered rings [3]. Other triphosphides MP_3 (M = Ca, Sr and Eu) consist of two-dimensional (2D) corrugated layers of either fused 6- and 22-membered rings or fused 14-membered rings [4–6]. The phosphorus tubes of pentagonal cross-section as basic building blocks occur in Hittorf's phosphorus [7] and KP_{15} [8]. The 2D sheets $^2_\infty[P_{10}]^{2-}$ originated through the connection of 1D pentagonal phosphorus tubes have been observed in the structures of BaP_{10} [9] and TlP_5 [10]. LiP_5 contains parallel oriented 1D bands of condensed six-membered rings that are connected via two-bonded phosphorus atoms to form an open three-dimensional (3D) $^2_\infty[P_5]^{1-}$ network [11].

During our investigation of the binary M–P (M = Ca, Sr, Ba, and La) systems using a high-pressure technique, we have unexpectedly obtained three new members of this class of compounds: α-SrP_3, BaP_8, and LaP_5, whose structures range from extended 2D layer to 3D framework and are characterized by the presence of both two- and three-fold homonuclear bonded phosphorus atoms with interesting bonding modes. In this paper we report on their preparation and crystal structures.

2. Experimental

2.1. Preparation of single crystals

For the preparation of α-SrP_3, 0.028 g (0.320 mmol) of strontium metal plate (99%, Katayama Chemical) and

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doi:10.1016/S0022-4596(03)00142-7

0.050 g (1.614 mmol) of red phosphorus powder (99%, Katayama Chemical) were weighed in a glove box under an atmosphere of argon. The mixture was filled in a hexagonal boron nitride (h-BN) crucible (typically 5 mm in inner diameter, 1.5 mm in thickness, and 4.5 mm in depth), which was surrounded by a cylindrical graphite tube heater. The h-BN crucible was calcined in a stream of nitrogen at 1200°C for 2 h to remove the adsorbed water prior to the use. The sample assembly was set in a cube ($2.0 \times 2.0 \times 2.0\,\mathrm{cm}^3$) made of pyrophyllite and subjected to high pressure using a cubic multianvil type apparatus (Riken, model CP-10). The reaction temperature was monitored by a thermocouple placed under the BN cell in the cube. Under an applied pressure of 3 GPa, the sample was rapidly heated at a rate of 38°C/min to 950°C. It was annealed at that temperature for 1 h, then cooled down to 750°C at a rate of 100°C/h, followed by quenching to room temperature prior to releasing the pressure. Black α-SrP_3 crystals with metallic luster were obtained in about 80% yield. The remaining product was found to be a small amount of black P based on powder X-ray diffraction (XRD) measurements using graphite monochromated Cu$K\alpha$ radiation. The crystals showed an irregular plate-like habit with various sizes ranging from 0.1 to 0.2 mm in diameter and several tenths of a millimeter in thickness. They were isolated mechanically from the reaction product for the further characterization by single-crystal XRD measurements.

The crystals of BaP_8 were prepared in the same way, except that the starting materials contained 0.035 g (0.255 mmol) Ba and 0.040 g (1.291 mmol) P and the annealed temperature was 1000°C. Irregular-shaped black crystals of BaP_8 were obtained in about 70% yield and the by-product accompanying BaP_8 was Ba_3P_2 that was confirmed by powder X-ray analysis. Attempts to prepare the isostructural Ca and Sr analogs, "MP_8 (M = Ca, Sr)", have so far been unsuccessful, possibly because Ca^{2+} and Sr^{2+} are too small to stabilize this structure type. The reaction of a stoichiometric Ca (Sr) and P elements at 3 GPa 1000°C for 1 h always resulted in the formation of Ca_3P_2 (SrP) and black P.

LaP_5 was synthesized from a stoichiometric reaction containing 0.052 g (0.374 mmol) La and 0.058 g (1.872 mmol) P. The sample was kept at 3 GPa 900°C for 2 h. Black plate-like crystals were obtained from the reaction product.

All three compounds appear to be relatively stable in air and water. Direct reaction of a stoichiometric mixture of the elemental components (Sr + 3P or Ba + 8P) at 3 GPa 950°C for 1 h yielded their respective single-phase polycrystalline samples, further confirming the existence of these phases.

Magnetic measurements were performed on the powder sample in the temperature range 2–300 K using a SQUID magnetometer (Quantum Design MPMS-5) under a field of 1 T.

2.2. Structure determination

X-ray data collections were carried out at room temperature (298 K) on an automated Rigaku AFC7R four-circle diffractometer using monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71073\,Å$). Cell dimensions were obtained from a least-square refinement with 25 automatically centered reflections in the range $30.24° \leqslant 2\theta \leqslant 42.94°$ for α-SrP_3, $30.80° \leqslant 2\theta \leqslant 44.21°$ for BaP_8, and $30.64° \leqslant 2\theta \leqslant 42.46°$ for LaP_5. Three standard reflections were re-measured after every 150 reflections. No decay was observed except the statistic fluctuation in a range of $\pm 0.97\%$ for α-SrP_3, $\pm 2.12\%$ for BaP_8, and $\pm 1.89\%$ for LaP_5. The raw intensity data were corrected for Lorentz and polarization effects, and for absorption by empirical method based on ψ-scan data.

The crystal structures were solved by Patterson methods and refined in SHELX-97 system [12] by full-matrix least-squares methods on F_o^2. For α-SrP_3, after introduction of anisotropic displacement parameters for all atoms the refinement of 22 parameters with 471 observed reflections. $[I \geqslant 2\sigma(I)]$ resulted in the residuals of $R_1/wR_2 = 0.0684/0.1180$. The reliability factors for the compound BaP_8 (LaP_5) converged to $R_1/wR_2 = 0.0476/0.1255$ (0.0391/0.1034) for 2702 (1272) observed reflections and 82 (31) variables. The final difference electron density maps were featureless in all cases, with the highest electron density less than $2.68\,e\,Å^{-3}$ at positions which are very close to the heavy atomic sites. Details of crystal parameters, data collection and structure refinements are given in Table 1 and the atomic coordinates and the equivalent isotropic displacement parameters are summarized in Table 2.

Table 1
Crystallographic data for α-SrP_3, BaP_8, and LaP_5

Formula	SrP_3	BaP_8	LaP_5
Formula weight	180.53	385.10	293.76
Crystal size (mm)	$0.20 \times 0.08 \times 0.04$	$0.13 \times 0.10 \times 0.015$	$0.18 \times 0.04 \times 0.01$
Space group	$C2/m$ (No. 12)	$P-1$ (No. 2)	$P2_1/m$ (No. 11)
a (Å)	9.199(6)	6.762(2)	4.885(1)
b (Å)	7.288(3)	7.233(2)	9.673(3)
c (Å)	5.690(3)	8.567(2)	5.577(2)
α	90°	86.32(2)°	90°
β	113.45(4) °	84.31(2)°	105.32(2)°
γ	90°	70.40(2)°	90°
V, (Å^3), Z	350.0(3), 4	392.6(2), 2	254.2(1), 2
d_{calc} (g/cm^3)	3.426	3.258	3.838
λMo$K\alpha$ (Å)	0.71073	0.71073	0.71073
μ (mm^{-1})	16.493	6.587	9.797
$2\theta_{\max}$	70°	70°	80°
Total reflections	857	3942	1806
Unique reflection	809	3445	1641
Observed $[I \geqslant 2\sigma(I)]$	471	2702	1272
No. of variables	22	82	31
GOF on F_o^2	0.933	1.025	1.061
R_1/wR_2 $[I \geqslant 2\sigma(I)]$	0.0684/0.1180	0.0476/0.1255	0.0391/0.1034
R_1/wR_2 (all data)	0.1249/0.1382	0.0710/0.1371	0.0597/0.1114

Table 2
Atomic coordinates, equivalent isotropic displacement parameters (Å^2) for α-SrP_3, BaP_8, and LaP_5

Atoms	x	y	z	U_{eq}
α-SrP_3				
Sr	0.3382(1)	0	0.1477(2)	0.0237(3)
P1	0.1404(2)	0.2560(2)	0.3205(3)	0.0219(4)
P2	0.0105(3)	0	0.3094(5)	0.0212(5)
BaP_8				
Ba	0.26154(5)	0.33805(4)	0.68142(3)	0.01879(9)
P1	0.0169(2)	0.0400(2)	0.6188(2)	0.0169(2)
P2	0.0891(2)	0.1864(2)	0.2408(2)	0.0169(2)
P3	0.1402(2)	0.0525(2)	0.0011(1)	0.0165(2)
P4	0.2333(2)	0.6766(2)	0.3948(2)	0.0206(2)
P5	0.2378(2)	0.5782(2)	0.1541(2)	0.0188(2)
P6	0.3980(2)	0.1203(2)	0.3306(2)	0.0179(2)
P7	0.4036(2)	0.7764(2)	0.0393(1)	0.0169(2)
P8	0.5269(2)	0.3300(2)	0.2036(2)	0.0168(2)
LaP_5				
La	0.45164(8)	1/4	0.12384(6)	0.0236(1)
P1	−0.1211(2)	0.0899(1)	0.5371(2)	0.0198(2)
P2	−0.2063(3)	0.0420(1)	0.8909(2)	0.0271(2)
P3	0.2097(3)	1/4	0.5715(3)	0.0213(2)

Note: U_{eq} is defined as one-third of the trace of the orthogonalized **U** tensor.

3. Results and discussion

3.1. α-SrP_3

In a previous work [5], Dahlmann et al. reported a SrP_3 phase which we call the β-phase here. The SrP_3 phase found in this work will be assigned as the α-form, according to the definition given by Bauhofer et al. for EuP_3 [6]. α-SrP_3 is isostructural with $SrAs_3$ and at least four compounds have been reported to adopt this structure type, including $BaAs_3$, $SrAs_3$, $EuAs_3$, and α-EuP_3 [1,2]. The crystal structure consists of 2D infinite, puckered polyanionic layers $^{2}_{\infty}[P_3]^{2-}$ that stack along the c-axis forming channels in the [010] direction into which the strontium cations are inserted, as shown in Fig. 1. The crystal structures of both α- and β-SrP_3 modifications are closely related to that of the orthorhombic black phosphorus [13] and can be derived from the latter by removing $\frac{1}{4}$ of the P atoms in different ways (Fig. 2). The black phosphorus is well known to be a layer structured compound composed of condensed P_6 rings in a chair-conformation. The removal of a part of P atoms from the layers and the transfer of metal valence electrons to the non-metal valence states will

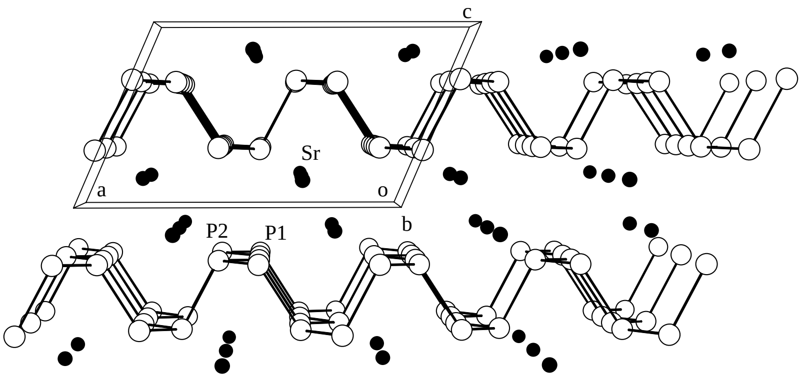

Fig. 1. The perspective projection of the α-SrP_3 structure along the monoclinic [010] direction. Large open circles: P; small black circles: Sr atoms.

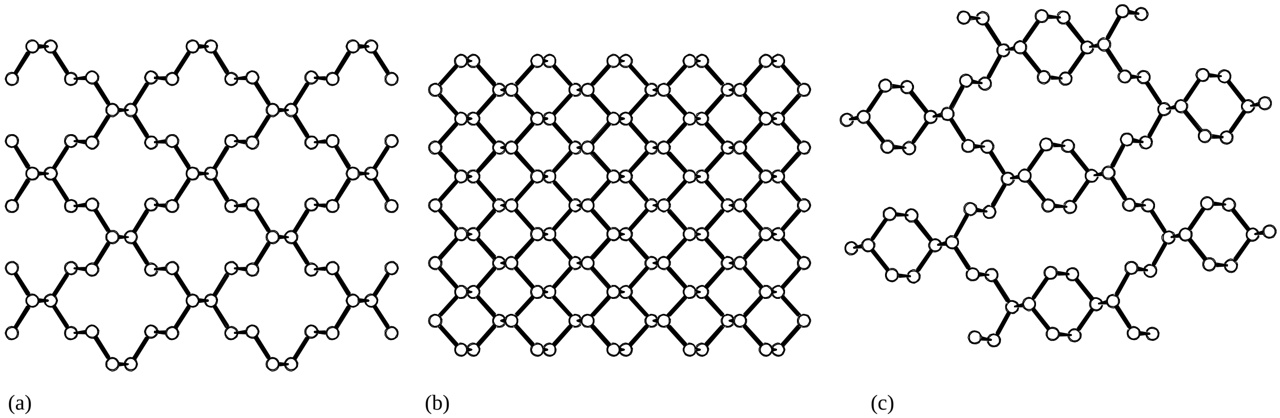

Fig. 2. The (001) projection of the phosphorus substructure in α-SrP_3 (a) as compared with the closely related structures in black phosphorus (b) and β-SrP_3 (c).

Table 3
Selected bond lengths (Å) and angles (deg) for α-SrP$_3$, BaP$_8$, and LaP$_5$

α-SrP$_3$			
Sr–P1 × 2	3.030(2)	P1–P2	2.203(2)
Sr–P1 × 2	3.112(2)	P1–P1	2.229(4)
Sr–P2	3.227(3)	P2–P1 × 2	2.203(2)
Sr–P1 × 2	3.273(2)	P2–P2	2.253(5)
Sr–P1 × 2	3.447(2)		
P2–P1–P1	106.0(1)	P1–P2–P2 × 2	103.1(1)
P1–P2–P1	115.8(1)		
BaP$_8$			
Ba–P1	3.223(1)	P3–P7	2.217(2)
Ba–P4	3.327(2)	P3–P3	2.269(3)
Ba–P7	3.332(2)	P3–P2	2.272(2)
Ba–P6	3.343(2)	P4–P1	2.181(2)
Ba–P4	3.381(2)	P4–P5	2.219(2)
Ba–P6	3.384(2)	P5–P4	2.219(2)
Ba–P5	3.398(2)	P5–P8	2.222(2)
Ba–P8	3.416(1)	P5–P7	2.227(2)
Ba–P4	3.509(2)	P6–P8	2.175(2)
Ba–P3	3.522(2)	P6–P2	2.187(2)
Ba–P2	3.523(2)	P7–P8	2.216(2)
P1–P4	2.181(2)	P7-P3	2.217(2)
P1–P1	2.205(3)	P7–P5	2.227(2)
P1–P2	2.238(2)	P8–P6	2.175(2)
P2–P6	2.187(2)	P8–P7	2.216(2)
P2–P1	2.238(2)	P8–P5	2.222(2)
P2–P3	2.272(2)		
P4–P1–P1	93.71(8)	P4–P5–P8	87.66(7)
P4–P1–P2	112.52(8)	P4–P5–P7	94.78(7)
P1–P1–P2	99.17(8)	P8–P5–P7	96.10(7)
P6–P2–P1	98.74(7)	P8–P6–P2	103.74(7)
P6–P2–P3	107.72(7)	P8–P7–P3	99.57(7)
P1–P2–P3	98.61(7)	P8–P7–P5	101.54(7)
P7–P3–P3	102.96(8)	P3–P7–P5	102.44(7)
P7–P3–P2	100.97(7)	P6–P8–P7	103.69(7)
P3–P3–P2	102.71(9)	P6–P8–P5	102.18(7)
P1–P4–P5	99.11(7)	P7–P8–P5	95.43(7)
LaP$_3$			
La–P3	2.994(2)	P1–P1	2.204(2)
La–P3	3.031(2)	P1–P3	2.209(2)
La–P2 × 2	3.061(1)	P2–P1	2.171(2)
La–P1 × 2	3.086(1)	P2–P2	2.215(3)
La–P2 × 2	3.110(1)	P3–P1 × 2	2.209(2)
P1–P2	2.171(2)		
P2–P1–P1	104.08(7)	P1–P2–P2	102.27(7)
P2–P1–P3	112.48(6)	P1–P3–P1	88.97(8)
P1–P1–P3	98.80(7)		

give rise to bond breaks and the formation of additional lone pairs. In β-SrP$_3$ half of the P$_6$ rings remain complete and the layers are built up of equal amounts of six-membered and 22-membered rings, while in α-SrP$_3$ all of the P$_6$ rings are opened yielding the uniform 14-membered rings. Despite the differences in the anionic layer geometry, the coordination environments around cations are quite similar in both polymorphs. The Sr atoms have a nine-fold coordination in a mono-capped square prism with comparable Sr-P distances: 3.030(2)–3.447(2) Å (average 3.217 Å, Table 3) in the α-phase vs. 3.047–3.578 Å (average 3.250 and 3.219 Å, respectively, depending on two different Sr sites) in the β-phase [5]. There are two distinct sites for P atoms in the α-form, of which P1 is bonded to two P and four additional Sr atoms in a distorted octahedral coordination, and P2 bonded to three P and one additional Sr in a tetrahedral arrangement. The P–P distances of 2.203(2)–2.253(5) Å are very reasonable when compared with 2.22–2.25 Å in the black phosphorus [13] and 2.188–2.282 Å in β-SrP$_3$ [5]. The P–P–P angles of 103.1(1)–115.8(1)° are in good agreement with those generally found for polyphosphide structures.

It is worth noting that EuP$_3$ was reported to be dimorphic with a phase transition at 960 K. The high-temperature phase, α-EuP$_3$, is isotructural to EuAs$_3$ and can be quenched as a metastable form and is stabilized at room temperature by adding a small amount of As (2%), while the low-temperature modification, β-EuP$_3$, has a slightly modified crystal structure involving the catenation of the P atoms [6]. α-EuP$_3$ has a slightly larger density than β-EuP$_3$ (4.825 and 4.764 g/cm^3, respectively). A similar situation is observed in the strontium analog. β-SrP$_3$ with the β-EuP$_3$ structure can be prepared by annealing stoichiometric amounts of elements in evacuated silica tubes at 1150°C and ambient pressure [5], while the α-SrP$_3$ reported here should be characterized as a higher density phase (3.426 vs. 3.411 g/cm^3 in β-SrP$_3$) and theoretically could be obtained by the transformation of the β-form under high-pressure and high-temperature (HPHT) conditions. The successful HPHT synthesis of single crystals of α-SrP$_3$ has confirmed this point.

3.2. BaP$_8$

BaP$_8$ represents a new structure type in which the phosphorus atoms form a three-dimensionally infinite polyanionic framework $^{3}_{\infty}[\mathrm{P}_8]^{2-}$ accommodating the barium cations as shown in Fig. 3. The 3D $^{3}_{\infty}[\mathrm{P}_8]^{2-}$ network can be considered as being built of 2D sheets in the following way (see Fig. 4): within the (101) plane of the triclinic unit cell, the phosphorus atoms are linked to form the six-membered rings in a chair-conformation and 10-membered rings with a double boat configuration. One P$_{10}$- and two P$_6$-cycles are condensed to produce the subunit P$_{16}$ which may be viewed as the building unit of the whole structure. Each P$_{16}$-subunit is connected to four translationally generated neighbors via P1–P1 and P5–P8 bonds to generate a corrugated 2D sheet $^{2}_{\infty}[\mathrm{P}_{16}]^{4-}$. Applying the *inversion-center* operations at the cell center or corners to this layer produces the neighboring equivalent layers along the [101] direction (see Fig. 3). These layers are held together through interlayer P3–P3 bridges resulting in the formation of the final 3D $^{3}_{\infty}[\mathrm{P}_8]^{2-}$ framework. The 3D network contains intersecting open channels running parallel to

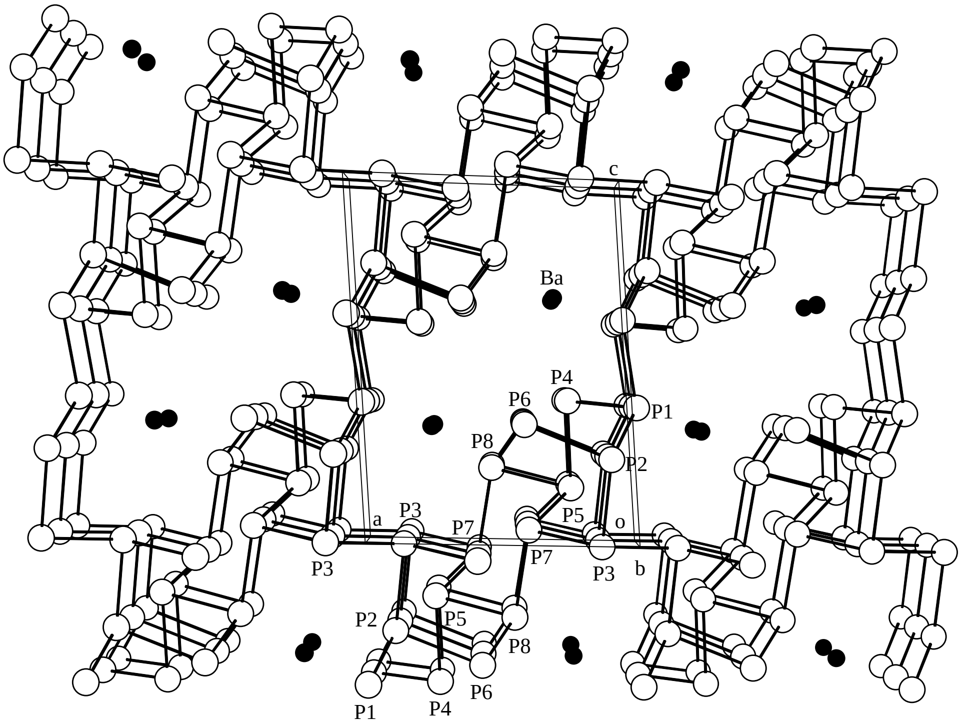

Fig. 3. Perspective view of the BaP_8 structure along the *b*-axis showing the channels occupied by the barium centers. The open channels also run along the *c*-axis and they have not been drawn for simplicity.

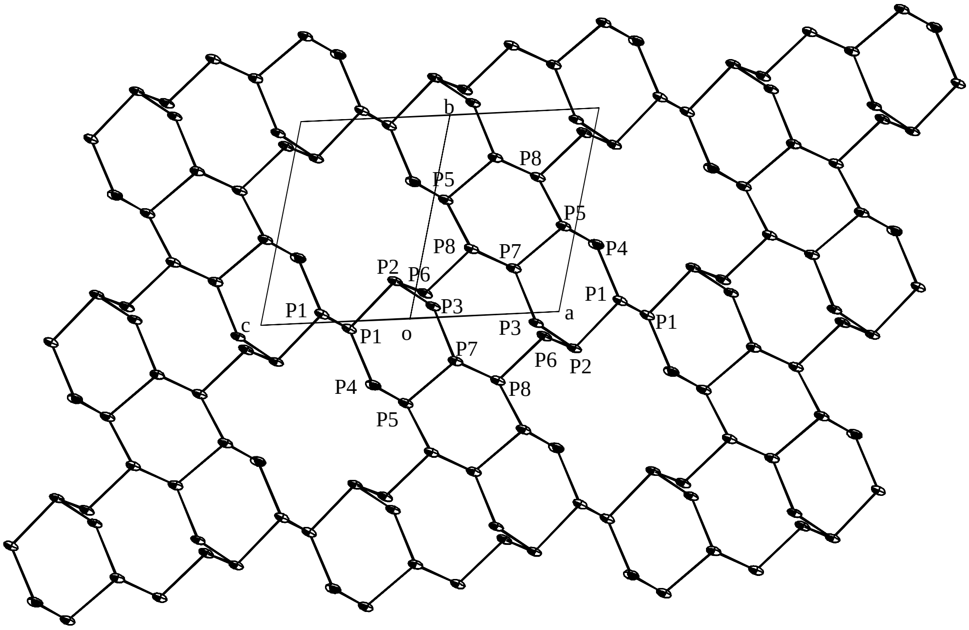

Fig. 4. An ORTEP representation of the ${}^{2}_{\infty}[P_{16}]^{4-}$ 2D sheet to show the atomic labeling scheme. The sheet is projected along the triclinic [101] direction. Displacement ellipsoids are drawn at the 50% probability level.

the [010] and [001] directions. The channels have an irregular cross section with dimensions of about 3.448×8.923 Å along the *b* and 3.329×7.907 Å along the *c* direction, respectively. Two rows of Ba^{2+} cations reside in the channels and each Ba^{2+} ion is eleven-coordinate to phosphorus in a highly distorted monocapped pentagon antiprismatic geometry, with Ba–P distances of 3.223(1)–3.523(2) Å (average 3.396 Å, Table 3), which agrees well with those observed in Ba_3P_{14} (average 3.476 Å, CN = 11) [5] and BaP_{10} (average 3.510 Å, CN = 12) [9]. P_6-cycles are well known in polyphosphide chemistry and the condensed P_{10}-cycles occur only in limited examples with crystal formula of MP_2 (M = Cu, Ag) and MP_4 (M = Mg, Cd,

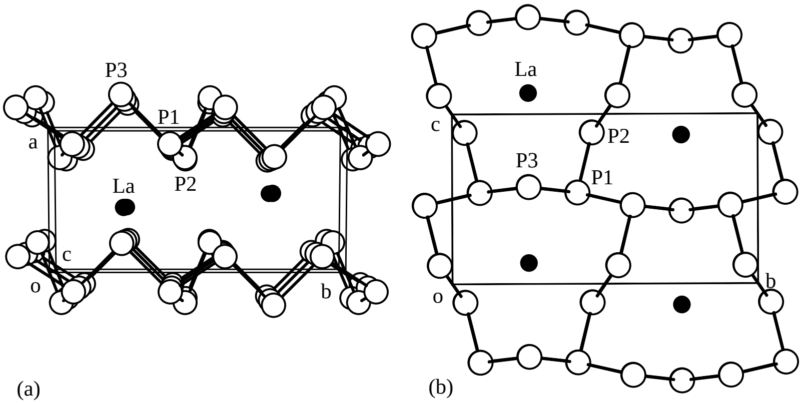

Fig. 5. Perspective view (a) and projection (b) of the LaP_5 structure along the [001] and [100] direction, respectively.

Cr, Re, Os, Mn, Fe, W) ([2] and references therein), while the compounds composed of the condensed both 6- and 10-membered rings of phosphorus atoms have not been observed before.

BaP_8 belongs to the family of Zintl phases; all the P atoms can fulfill the octets. There are eight crystallographically independent P atoms, six of which (P1, P2, P3, P5, P7, and P8) form three covalent P–P bonds and thus are considered to be formally neutral [(3b)P^0]. In contrast P4 and P6 are connected to only two neighboring P atoms and therefore carry a formal negative charge [(2b)P^{1-}]. The three-bonded, (3b)P^0, atoms have in addition to their homoatomic neighbors one additional Ba^{2+} neighbor situated in the lone-pair direction. The P–P–P bond angles vary from 87.66(7) to 112.52(8)°, which is within the allowable range for sp^3 hybridized bond angles consistent with a covalent character. The two-bonded, (2b)P^{1-}, atoms have two or three Ba^{2+} positions as additional neighbors which together with the homonuclearly bonded P atoms are arranged in a distorted tetrahedral and trigonal-bipyramidal geometry around P6 and P4, respectively. The P–P distances of 2.175(2)–2.272(2) Å listed in Table 3 are close to the single bond distances of 2.22–2.25 Å in the layer of the black phosphorus [13], and the corresponding distances in other polyphosphides such as BaP_3 (2.16–2.30 Å) (3), Ba_3P_{14} (2.154–2.294 Å) (5), BaP_{10} (2.150(3)–2.245(2) Å) (9), and α-SrP_3 (2.203(2)–2.253(5) Å) mentioned above.

3.3. LaP_5

The newly high-pressure prepared LaP_5 forms a layer structure in which puckered polyanionic layers of condensed P_{12} rings alternate with layers of lanthanum atoms along the [100] direction, as shown in Fig. 5. The high-pressure LaP_5 phase present here is isostructural with NdP_5 [14], but differs from the LaP_5 phase reported by Wichelhaus et al. [14] in that the latter is a superstructure variant with $a' = 2a$. We have examined our crystals of LaP_5 on a Rigaku RAXIS imaging plate area detector. The overexposed oscillation images revealed no supercell reflections. It is noted that the LnP_5 (Ln = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) prepared under ambient-pressure adopt three kinds of very similar 2D structures [2], of which the unit cell volumes of the La and Ce phases are twice of those of the others, the compounds from Nd to Lu series are isotypical with the newly prepared LaP_5, and β-YbP_5 forms a more closely packed variant of the above structures. In this family, when the ionic size decreases from La to Lu, the 2D polyanionic net appears to adjust its detailed shape so as to fit the decreasing size of the cation by altering the P–P bond lengths and conformational angles. Such a structural modification has been interpreted as being similar to the effect of the application of pressure [2] and this has been confirmed by the present study. Under high-pressure the size of La^{3+} is slightly reduced, therefore a structure change is understandable. The observed average La–P bond length of 3.067 Å (Table 3) in this study is indeed slightly smaller than that (average La–P = 3.071 Å) reported by Wichelhaus et al. [14] for the LaP_5 ambient-pressure phase. The P–P distances and P–P–P angles cover the similar ranges (2.171(2) 2.215(3) Å and 88.97(8)–112.48(6)° in this work vs. 2.168(3)–2.216(3) Å and 86.0(1)–113.9(1)° by Wichelhaus et al.).

All three compounds are valence compounds, $[Sr^{2+}(P^0)_1(P^{1-})_2]$, $[Ba^{2+}(P^0)_6(P^{1-})_2]$, and $[La^{3+}(P^0)_2(P^{1-})_3]$, in a classical sense and all valence electrons are in localized states, therefore, they should be insulators or semiconductors. The magnetic susceptibility measurements have confirmed this point. α-SrP_3, BaP_8, and LaP_5 have all been found to be diamagnetic with the observed susceptibility values $\chi_{mol} = -1.397 \times 10^{-5}$, -1.069×10^{-4} and -4.979×10^{-5} emu/mol, respectively.

Acknowledgments

This study has been supported by Grant-in-Aid for Scientific Research (B) (No. 14350461) and the COE

Research (No. 13CE2002) of the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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