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$Ba_{11}KX_7O_2$ (X = P, As): Two Novel Zintl Phases with Infinite Chains of Oxygen Centered Ba_6 Octahedra, Isolated X^{3-} and Dimeric X_2^{4-} Anions

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Abstract. Reactions of "BaX" (X = P, As) with Ba, K and BaO in tantalum tubes at 900–1000 °C yielded black, very air- and moisture-sensitive crystals of $Ba_{11}KP_7O_2$ and isotypic $Ba_{11}KAs_7O_2$ which were characterized by EDX and X-ray diffraction (orthorhombic, *Fddd*, $Z = 8$; $a = 1069.9(1)$, $b = 1514.3(2)$, $c = 3164.6(4)$ pm and $a = 1087.8(2)$, $b = 1542.3(2)$, $c = 3232.4(4)$ pm, respectively). The structure contains infinite zigzag chains, ${}^{1}_{\infty}[Ba_4Ba_{2/2}O]$, of oxygen-centered, corner-sharing Ba_6 octahedra along [100]. They are connected by linear strings built of alternating isolated X atoms and X_2 dimers to form layers parallel to (001). While the isolated X atoms are surrounded by eight Ba forming a distorted cube, the X_2 dimers center a Ba_{12} polyhedron which is comprised of a pair of face-sharing Ba square antiprisms. This results in a cube–antiprism-antiprism–cube sequence of face-sharing Ba polyhedra. Additional X atoms function as spacers between the layers and connect them along [001]. Two atom positions are statistically occupied by Ba and K, and the formula may be written as $Ba^{2+}_{11}K^{+}X^{3-}_{5}(X_2)^{4-}O^{2-}_{2}$ according to the Zintl-Klemm concept.

Keywords: Solid State Chemistry; Crystal Structure; Zintl Phases; Oxides; Phosphides; Arsenides

$Ba_{11}KX_7O_2$ (X = P, As): Zwei neuartige Zintl-Phasen mit unendlichen Ketten sauerstoffzentrierter Ba_6-Oktaeder, isolierten X^{3-} und dimeren X_2^{4-} Anionen

Inhaltsübersicht. Reaktionen von „BaX" (X = P, As) mit elementarem Ba, K und BaO in Tantalampullen bei 900–1000 °C ergaben schwarze, sehr luft- und feuchtigkeitsempfindliche Kristalle von $Ba_{11}KP_7O_2$ und der dazu isotypen Verbindung $Ba_{11}KAs_7O_2$, welche durch EDX und Röntgenbeugung charakterisiert wurden (orthorhombisch, *Fddd*, $Z = 8$; $a = 1069{,}9(1)$, $b = 1514{,}3(2)$, $c = 3164{,}6(4)$ pm und $a = 1087{,}8(2)$, $b = 1542{,}3(2)$, $c = 3232{,}4(4)$ pm). In der Struktur liegen parallel zu [100] unendliche Zickzack-Ketten, ${}^{1}_{\infty}[Ba_4Ba_{2/2}O]$, aus eckenverknüpften Ba_6-Oktaedern vor, die durch O-Atome zentriert werden. Dazwischen befinden sich lineare Reihen von abwechselnd angeordneten isolierten X-Atomen und X_2-Hanteln, welche die Oktaederketten zu Schichten parallel zu (001) miteinander verbinden. Während sich die X-Atome in einem verzerrten Ba_8-Würfel befinden, zentrieren die X_2-Hanteln einen Ba_{12}-Polyeder, welcher aus einem Paar flächenverknüpfter, quadratischer Ba-Antiprismen aufgebaut ist. Hieraus ergibt sich die Abfolge Würfel-Antiprisma-Antiprisma-Würfel aus flächenverknüpften Ba-Polyedern. Zwischen den Schichten befinden sich weitere isolierte X-Atome und verknüpfen diese entlang [001] miteinander. Zwei Atompositionen sind statistisch mit Ba und K besetzt, so daß nach dem Zintl-Klemm-Konzept die Summenformel der Verbindungen auch durch $Ba^{2+}_{11}K^{+}X^{3-}_{5}(X_2)^{4-}O^{2-}_{2}$ ausgedrückt werden kann.

Introduction

Guided and inspired by the Zintl-Klemm concept [1, 2], an intriguing variety of compounds with novel structures and interesting properties could be discovered during the past 60 years [3–5 (and references therein)]. The majority of these compounds are com-

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prised of an electropositive alkali, alkaline-earth or rare-earth metal and group 13 to 15 elements. In the course of all these experiments and investigations, a number of compounds was synthesized that could not be structurally rationalized by the Zintl-Klemm concept but seemed to violate its valence rules because of their 'excess' of electropositive metal and therefore surplus electrons. Some of them, for example, the phases A_2X (A = Ca, Sr, Ba; X = As, Sb, Bi) [6–12] or A_5X_3 (A = Ca, Sr, Eu, Yb; X′ = Sb, Bi; orthorhombic, Yb_5Sb_3 structure type) [13–20] later turned out to be ternary compounds A_4X_2O [21–27] (tetragonal, K_2NiF_4 structure) and A_5X_3H [28] containing oxygen and hydrogen, respectively. Other compounds such as $Ba_{10}Ge_7O_3$ [29], $Na_3Sr_7(P_3)_3O$ [30] or $Cs_6[SnAs_3]O_{0.5}$ [31] were first discovered in reactions contaminated by adventitious impurities and later obtained in high yields by intentionally adding oxygen-containing starting materials. In addition $Na_{24}In_5O_{15}$ [32] was serendipitously synthesized by reaction of 'NaIn', Na_2O and Na_2O_2. Compounds like $Ba_{21}X_2O_5$ (X = Si, Ge) [33] have surplus electrons and therefore are preferably termed suboxides rather than Zintl phases.

Presented here are the first results of our research to obtain novel Zintl compounds that contain also oxygen in their structure.

Experimental Section

Synthesis. Several reagents and the products are highly sensitive to air and moisture and their handling required an inert atmosphere and high vacuum techniques. Accordingly, all reactions were loaded in argon-filled glove boxes. Tantalum or niobium was used as material for the reaction containers, which were prepared from metal tubing by welding them in an argon-filled arc-welder. After the reactions were loaded the sealed metal containers were encapsulated in fused silica jackets under vacuum. Reagents employed were Ba (Aldrich, 99%), K (Ventron, 99.9%), P (Hoechst AG, ultrapure), As (Ventron, 99.5%) and $BaCO_3$ (Alfa, 99.8%). BaO was obtained by decomposing $BaCO_3$ in corundum crucibles under high vacuum at 1000 °C. P and As were prereacted to "BaP" and "BaAs" in tantalum tubes at 900 °C. The multiphase products were analyzed by energy-dispersive X-ray analysis (EDX) and atom-emission spectroscopy with inductively coupled plasma (AES-ICP) but no significant amounts of impurities, such as Ta from the reaction containers or Sr as a common impurity in Ba, could be detected. Mixtures of Ba, K, BaO and "BaX" (X = P, As) with a molar ratio of 4:2:2:8 were heated at 900 °C for 5 days and cooled at 10 °C h^{-1} to 400 °C, and then the furnace was turned off. The products were black crystals of the new phases $Ba_{11}KP_7O_2$ (70%) and $Ba_{11}KAs_7O_2$ (50%), respectively, in addition to Ba_4X_2O (20–30%) [24, 26] and unidentified phases. A surplus of Ba and K seemed to be necessary for the formation of the new compounds since reactions loaded with the exact stoichiometry gave much lower yields of the desired product and more Ba_4X_2O instead. Experiments without K yielded Ba_4X_2O only. EDX analysis of some crystals confirmed the K content of the two new phases. Subsequent reactions with Sb instead of As or P yielded an unidentified phase as well as Ba_4Sb_2O [25], while runs with Bi gave the new compound $Ba_{11}Bi_{10}$ [34] ($Ca_{11}Sb_{10}$ structure type [35]) as well as Ba_4Bi_2O [27].

X-ray Studies. Crystals of $Ba_{11}KP_7O_2$ and $Ba_{11}KAs_7O_2$ were mounted separately in thin-walled glass capillaries in the glove box and their quality was checked by Laue photographs on precession cameras. Through precession photographs of the zeroeth to the third layers of suitable crystals of both compounds, the Laue symmetry as well as the systematic reflection absences were found to be characteristic of the unique space group *Fddd* (no. 70; the origin choice 2 was later used for the structure refinement). Additional long-time-exposure photos excluded the possibility of a superstructure. The same crystals were used to determine the exact orthorhombic cell parameters and the orientation matrixes by a least-squares refinement of the setting angles of 20 centered reflections on a Stoe STADI4 diffractometer with graphite-monochromated Mo Kα radiation. All data were collected at room temperature for the space group *Fddd* ($4° \leq 2\theta \leq 55°$; $+h$, $+k$ $+l$ and Friedel opposites). An empirical absorption correction was applied to the full data set with the aid of 30 ψ-scans. For both compounds the data

Table 1 Crystallographic Data and Details of the Structure Determination for $Ba_{11}KP_7O_2$ and $Ba_{11}KAs_7O_2$

Compound	$\mathbf{Ba_{11}KP_7O_2}$	$\mathbf{Ba_{11}KAs_7O_2}$
Crystal data		
Crystal color, habit	black, irregular	
Crystal system, space group, Z	orthorhombic, *Fddd* (no. 70, origin choice 2), 8	
Lattice constants (pm)		
a	1069.9(1)	1087.8(2)
b	1514.3(2)	1542.3(2)
c	3164.6(4)	3232.4(4)
Volume (10^6 pm^3)	5127.2(7)	5421(1)
$\rho_{calculated}$ (g/cm^3)	4.66	5.16
Data collection		
Diffractometer	Stoe STADI4	
Radiation, monochromator	Mo Kα (λ = 71.073 pm), graphite	
Scan type	ω	
Octants measured	*h*, *k*, *l* and Friedel opposites	
Refinement		
Measured reflections	2946	3466
Independent reflections ($F > 3\sigma_F$)	1298	1337
Number of variables	54	54
Absorption correction	empirical, 30 ψ-scans	
Secondary extinction coefficient	$9(1) \times 10^{-5}$	$8(1) \times 10^{-5}$
R_{avg}	0.019	0.032
R [a]; Rw [b] ($F > 3\sigma_F$)	0.028; 0.044	0.040; 0.071
Largest residual peak (e/10^6 pm^3)	0.98 (127 pm from Ba3)	1.70 (186 pm from As1)

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$,

[b] $R_w = [\Sigma[w(F_o^2 - F_c^2)^2/\Sigma(F_o^2)^2]^{1/2}$; $w = \sigma_F^{-2}$

collection procedures were the same. The structure of $Ba_{11}KP_7O_2$ was determined using first direct methods (SHELXS-86 [36]) to obtain a structural model which was then employed for subsequent least-squares refinements and difference Fourier syntheses (SHELXL-93 [37]). The residuals after the anisotropic refinement of all atoms were $R(F) = 0.028$ and $Rw(F^2) = 0.044$ for $F_0 > 3\sigma(F_0)$. With the atom positions of $Ba_{11}KP_7O_2$ as starting parameters, the structure of $Ba_{11}KAs_7O_2$ was then determined as well ($R(F) = 0.040$ and $R_w(F^2) = 0.071$ for $F_0 > 3\sigma(F_0)$). The powder patterns calculated on the basis of the refined structures agreed very well with the observed ones. All yields were estimated according to the relative intensities of the powder pattern lines for each known phase present. Some data collection and refinement parameters are given in Table 1. The final atomic coordinates, isotropic-equivalent and anisotropic temperature factors and their standard deviations are listed in Tables 2–5. The structure factor data are available from the author.

Table 2 Positional and Displacement Parameters U_{eq} [a]) (pm^2) for $Ba_{11}KP_7O_2$ [b])

atom	position	x	y	z	U_{eq}
Ba1/K1 [b])	32*h*	0.41519(5)	0.99068(4)	0.55746(2)	295(2)
Ba2/K2 [b])	32*h*	0.31262(4)	0.74714(3)	0.68035(1)	233(2)
Ba3	16*g*	1/8	1/8	0.52957(2)	227(2)
Ba4	16*f*	1/8	0.42627(4)	1/8	183(2)
P1	32*h*	0.1294(2)	0.8970(1)	0.52316(6)	208(4)
P2	16*e*	0.5176(2)	1/8	1/8	171(5)
P3	8*a*	1/8	1/8	1/8	306(9)
O	16*g*	1/8	1/8	0.8760(3)	253(16)

[a]) $U_{eq} = 1/3\, \Sigma_i \Sigma_j U_{ij}\, a_i^*\, a_j^*\, a_i\, a_j$

[b]) The refined composition based on the single-crystal data was $Ba_{11.07(3)}K_{0.93}P_7O_2$. The statistical occupancy with Ba and K on the positions were: Ba1/K1: 80.0(4)% Ba and 20.0% K; Ba2/K2: 96.8(4)% Ba and 3.2% K (constrained to 100%).

Table 3 Displacement Parameters U_{ij} [a]) (pm^2) for $Ba_{11}KP_7O_2$

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba1/K1	275(3)	337(3)	273(3)	113(2)	37(2)	52(2)
Ba2/K2	251(3)	215(3)	233(3)	47(2)	17(2)	11(2)
Ba3	190(3)	316(4)	174(3)	–14(2)	0	0
Ba4	191(3)	170(3)	190(3)	0	5(2)	0
P1	219(9)	199(9)	206(8)	–8(7)	–33(7)	18(7)
P2	147(11)	174(11)	191(11)	0	0	9(9)
P3	247(21)	348(22)	323(22)	0	0	0
O	162(35)	294(40)	305(38)	47(31)	0	0

[a]) $U_{ij} = \exp\{-2\pi^2(U_{11}\, h^2\, a^{*2} + \cdots + 2\, U_{23}\, k\, l\, b^* c^*)\}$

Table 4 Positional and Displacement Parameters U_{eq} [a]) (pm^2) for $Ba_{11}KAs_7O_2$ [b])

atom	position	x	y	z	U_{eq}
Ba1/K1 [a])	32*h*	0.41546(7)	0.99077(5)	0.55841(2)	275(3)
Ba2/K2 [a])	32*h*	0.31367(6)	0.74991(4)	0.68065(2)	220(2)
Ba3	16*g*	1/8	1/8	0.53016(3)	209(2)
Ba4	16*f*	1/8	0.42555(5)	1/8	180(2)
As1	32*h*	0.1292(1)	0.89835(7)	0.52347(3)	196(3)
As2	16*e*	0.5092(1)	1/8	1/8	150(3)
As3	8*a*	1/8	1/8	1/8	303(5)
O	16*g*	1/8	1/8	0.8759(4)	341(26)

[a]) $U_{eq} = 1/3\, \Sigma_i \Sigma_j\, U_{ij}\, a_i^*\, a_j^*\, a_i\, a_j$

[b]) The refined composition based on the single-crystal data was $Ba_{10.94(3)}K_{1.06}As_7O_2$. The statistical occupancy with Ba and K on the positions were: Ba1/K1: 80.1(4)% Ba and 19.9% K; Ba2/K2: 93.5(4)% Ba and 6.5% K (constrained to 100%).

Table 5 Displacement Parameters U_{ij} [a]) (pm^2) for $Ba_{11}KAs_7O_2$

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba1/K1	272(5)	298(5)	253(4)	109(3)	20(3)	9(3)
Ba2/K2	248(4)	206(4)	207(4)	56(3)	15(3)	–9(3)
Ba3	194(4)	274(4)	158(4)	–17(3)	0	0
Ba4	221(4)	150(4)	168(4)	0	4(3)	0
As1	218(5)	194(5)	178(5)	3(4)	–35(4)	22(4)
As2	159(6)	138(6)	151(6)	0	0	–11(5)
As3	244(11)	380(13)	287(12)	0	0	0
O	359(66)	332(61)	333(57)	–70(53)	0	0

[a]) $U_{ij} = \exp\{-2\pi^2(U_{11}\, h^2\, a^{*2} + \cdots + 2\, U_{23}\, k\, l\, b^* c^*)\}$

Results and Discussion

$Ba_{11}KP_7O_2$ and the isotypic $Ba_{11}KAs_7O_2$ crystallize in the orthorhombic space group *Fddd* in form of black, irregularly-shaped crystals. Both compounds are very sensitive to moisture, in the presence of which they decompose immediately developing PH_3 and AsH_3, respectively. Reaction with water results in explosion and fire. The lattice constants and cell volumes are listed in Table 1 and show the expected increase from the P to the As compound.

The statistical occupancy of two atom positions with Ba and K ensures electronic neutrality, and makes possible an ionic formulation as $Ba^{2+}{}_{11}K^{+}X^{3-}{}_{5}(X_2)^{4-}O^{2-}{}_{2}$ according to the Zintl-Klemm concept. In both compounds the position Ba1/K1 (Wyckoff notation: 32*h*) was refined with about 80% Ba and 20% K while the position Ba2/K2 (32*h*) is statistically occupied by about 95% Ba and only 5% K (for the exact values with standard deviations for each compound see Tables 2 and 4). The attempted refinement of the positions Ba3 (16*g*) and Ba4 (16*f*) showed no significant K content. Therefore, the refined compositions of the two compounds were $Ba_{11.07(3)}K_{0.93}P_7O_2$ and $Ba_{10.94(3)}K_{1.06}As_7O_2$, respectively. The statistical occupancy of certain positions with Ba and K also concurs with the calculations of the Madelung part of lattice energy, MAPLE [38]

Table 6 Important Interatomic Distances for $Ba_{11}KP_7O_2$ and $Ba_{11}KAs_7O_2$

Distance	X = P	X = As	Distance	X = P	X = As
Ba1/K1–Ba1/K1	360.7(1)	367.7(3)	**X1**–Ba3	321.0(2)	328.3(2)
–Ba1/K1	407.4(1)	421.0(3)	–Ba3	345.9(2)	350.2(2)
–Ba2/K2	390.1(1)	396.0(2)	–Ba4	325.3(3)	330.9(1)
–Ba2/K2	391.0(1)	401.9(2)			
–Ba2/K2	427.4(1)	434.9(2)	**X2**–Ba1/K1 a)	354.0(2)	354.0(2)
–Ba3	381.5(1)	388.6(3)	–Ba2/K2 a)	336.1(2)	338.7(2)
–Ba4	389.4(1)	395.3(3)	–Ba3 a)	323.1(1)	331.4(1)
–Ba4	400.0(1)	405.1(3)	–Ba4 a)	322.1(1)	332.4(2)
Ba2/K2–Ba2/K2	409.6(1)	408.3(1)	–X2	229.8(5)	252.0(4)
–Ba3	374.9(1)	381.0(1)			
–Ba3	402.5(1)	409.7(2)	**X3**–Ba1/K1 b)	370.7(2)	375.7(2)
–Ba4	380.2(1)	384.5(2)	–Ba2/K2 b)	324.3(1)	334.1(2)
–Ba4	394.8(1)	400.3(2)			
Ba3–Ba4 a)	426.3(1)	434.3(2)	**O**–Ba1/K1 a)	277.3(6)	281(1)
			–Ba2/K2 a)	271.6(5)	273.9(9)
X1–Ba1/K1	321.8(2)	329.7(2)	–Ba4 a)	278.5(5)	282.9(8)
–Ba1/K1	350.1(2)	360.6(3)			
–Ba1/K1	354.1(2)	361.5(2)			
–Ba2/K2	336.3(2)	344.1(2)			
–Ba2/K2	339.6(2)	344.1(2)			
–Ba2/K2	402.8(2)	405.5(3)			

a) distance occurs twice
b) distance occurs four times

Table 7 $Ba_{11}KX_7O_2$: Madelung Part of Lattice Energy per Ba a) (MAPLE) in kJ/mol

atom	formal charge	MAPLE/atom (X = P)	MAPLE/atom (X = As)
Ba1/K1 a)	+2	802.5	795.3
Ba2/K2 a)	+2	869.4	856.0
Ba3	+2	938.1	910.5
Ba4	+2	959.4	918.0

a) The statistical occupancy with K was not taken into account. The formal charge of the anions used in this calculation was X1 = –3, X2 = –2, X3 = –3, O = –2.

(Table 7). Here the position of Ba1/K1 has the lowest contribution in terms of Coulombic energy of all Ba positions (each calculated with the formal charge 2+, neglecting the occupancy with K) and therefore is most favored for a statistical occupancy together with the lower charged K^+ followed by Ba2/K2, Ba3 and Ba4. In addition, all filmwork for both compounds indicated the same space group and lattice constants (without any hint of a superstructure) as determined also with the diffractometer data. Furthermore, attempted refinements in non-isomorphic subgroups (e.g., *F222, Fdd2*) did not resolve this disorder or give better results.

The structures of the new compounds may be described best in terms of the Ba/K polyhedra around the anions. Hereby the O atom centers a slightly distorted Ba_6 octahedron of three crystallographically distinct metal atoms. Two Ba1/K1 and two Ba2/K2 atoms form the equatorial plane while two Ba4 atoms constitute the apexes. The spread among the three different Ba/K–O distances within this octahedron is relatively small ($\bar{d}$ = 276 pm, Δ_{max} = 7 pm for $Ba_{11}KP_7O_2$

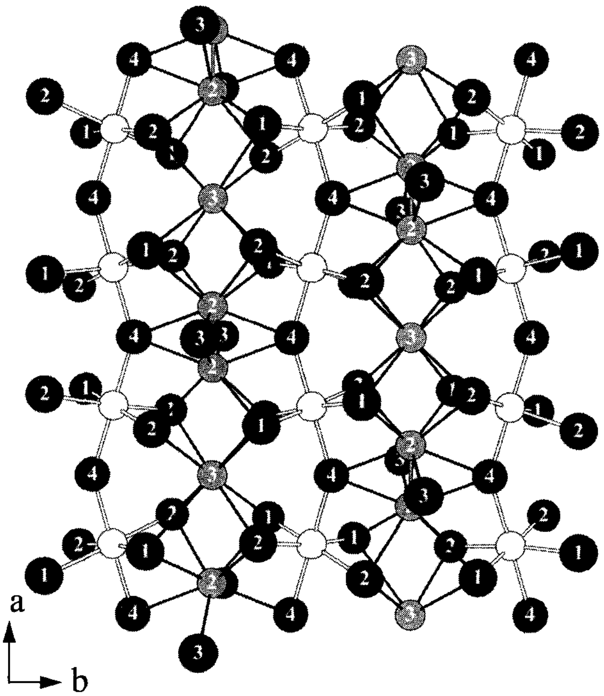

Fig. 1 $Ba_{11}KX_7O_2$: [001] view of one layer composed of infinite chains of oxygen centered $(Ba/K)_6$ octahedra and of the confacial columns with the cube-antiprism-antiprism-cube sequence of Ba polyhedra that are centered by X^{3-} and X_2^{4-} anions (dark gray: Ba/K, light gray: X (= P, As), empty spheres: O; the atoms are numbered crystallographically).

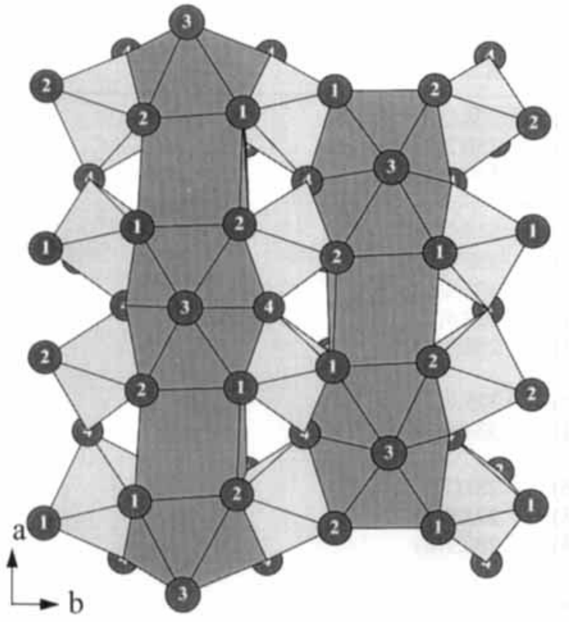

Fig. 2 The same layer as in Figure 1 but with the polyhedra emphasized.

and $\bar{d}$ = 279 pm, Δ_{max} = 9 pm for $Ba_{11}KAs_7O_2$). Important interatomic distances and their standard deviations are listed in Table 6. In general, these distances in the phosphorus compound are shorter than comparable ones in the arsenic compound. Figure 1 shows how the $(Ba/K)_6$ octahedra are linked over common Ba4 atoms into infinite, zigzag chains $^1_\infty[(Ba/K)_4Ba_{2/2}O]$ parallel to [100] in the unit cell. These chains are separated by linear strings built of alternatingly arranged isolated X3 atoms and $X2_2$ dimers. Each isolated X3 atom centers a distorted cube of four Ba1/K1 and four Ba2/K2 atoms, all of which also belong to the equatorial planes of the four adjacent $O(Ba/K)_6$ octahedra. Within this cube the distances Ba2/K2–X3 are much shorter (324 and 334 pm) than those of Ba1/K1–X3 (371 and 376 pm for X = P and As, respectively). The $X2_2$ dimer centers a $(Ba/K)_{12}$ polyhedron which is comprised of a pair of face-sharing Ba/K square antiprisms. Two Ba3 (that are not bonded to O but only to As or P) and two Ba4 atoms constitute the common face of the antiprisms and therefore bridge the X–X bond of the $X2_2$ unit in the center, while Ba1/K1 and Ba2/K2 atoms, form the top and bottom plane of the $(Ba/K)_{12}$ polyhedron. The P–P (230 pm) and As–As distances (252 pm) of the dumbbells are in good agreement with those in the structures of Ba_4P_3 (225 and 232 pm) [39] and Sr_4As_3 (252 and 255 pm) [40], respectively. The polyhedral arrangement results in columns along [100] with the confacial sequence cube-antiprism-antiprism-cube. In combination with the zigzag chains of oxygen centered $(Ba/K)_6$ octahedra, these columns form layers parallel to (001) (Figure 1 and 2). Figure 3 shows how these layers are piled up along [001] in the unit cell and shifted each time about $^1/_4$ $^1/_4$ $^1/_4$ relatively to each other. As illustrated in Figures 3 and 4, the As1 atoms are located between the layers in the center of $(Ba/K)_9$ polyhedra which are formed by six Ba/K atoms (2×Ba1/K1, 2×Ba2/K2, Ba3 and Ba4) of one layer and three Ba/K atoms (Ba1/K1, Ba2/K2 and Ba3) of the adjacent layer and vice versa. They so connect the layers into a three-dimensional network. The spread among the distances Ba/K–X in these $(Ba/K)_9X$ polyhedra is rather large, with distances ranging from 321 pm for Ba3–X1 to 402 pm for Ba2/K2–X1 for X = P ($\bar{d}$ = 347 pm) and from 328 pm to 406 pm for X = As ($\bar{d}$ = 351 pm).

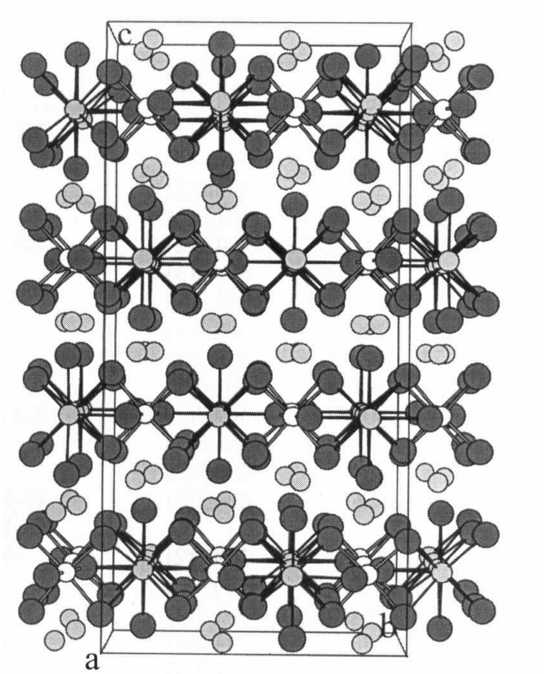

Fig. 3 $Ba_{11}KX_7O_2$: Perspective view of the unit cell to illustrate the stacking of the layers along [001]. A: the layer featured in Figures 1 and 2. B: a puckered layer of X1 atoms (atoms are marked as in Figure 1).

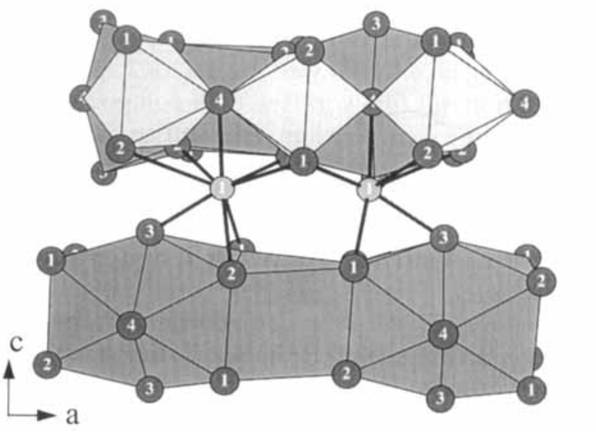

Fig. 4 $Ba_{11}KX_7O_2$: Part of the crystal structure to show how X1 atoms connect the layers along [001].

All Ba/K atoms center distorted octahedra of the anions O, X1, X2 or X3. Due to the sizeable difference of the Ba/K–O versus the Ba/K–X separations and the wide breadth of the latter as well as the short X2–X2 contacts, the polyhedra are highly distorted from the ideal octahedra symmetry. Ba1/K1 and Ba2/K2 atoms are each surrounded by three X1 and one X2, X3 and O atoms. Ba3 has four X1 and two X2 atoms (the $X2_2$ dimer) as nearest neighbors. The distortion becomes most obvious in the coordination environment of Ba4 which is formed by two X1 as apex atoms as well as two X2 and two O atoms that shape the equatorial plane of the octahedron. Within this plane one edge is formed by the X2 dumbbell with a short interatomic distance of 230 (X = P) and 253 pm (X = As) while the opposite edge is shaped by the O atoms with a much larger separation of 535 (X = P) and 544 pm (X = As). Therefore the equatorial plane of this octahedron resembles much more of a trapezium than a square (Figure 1).

The novel structure of $Ba_{11}KP_7O_2$ and of the isotypic $Ba_{11}KAs_7O_2$ is the first to contain infinite chains ${}^1_\infty[(Ba/K)_4Ba_{2/2}O]$, of corner-sharing and oxygen centered alkaline-earth metal octahedra. So far, Zintl phases that contain also oxygen are known as follows:

a) Isolated OA_6 octahedra occur in the structure of $Na_3A_7(P_3)_3O$ (hexagonal, *P6₃/mcm;* A = Sr, Eu) together with P_3^{5-} Zintl anions [30].

b) Layers ${}^2_\infty[A_2A_{4/2}O]$ of corner-sharing octahedra are the important feature of the large number of A_4X_2O representatives that crystallize in the K_2NiF_4 structure (tetragonal, *I4/mmm*; A = Ca, Sr, Ba, Eu, Yb; X = P, As, Sb, Bi [21–27]; Ba_4P_2O and Eu_4P_2O crystallize with an orthorhombic distortion in the space group *Cmca* [24, 41]). They all contain in addition isolated, noble gas isoelectronic X^{3-} anions.

c) A three-dimensional network ${}^3_\infty[A_{6/2}O]$ of corner-sharing octahedra and isolated X^{4-} anions are characteristic of A_3XO-type compounds that adopt either the $GdFeO_3$ (orthorhombic, *Pbnm*; A = Ca, Sr, Ba, Eu; X = Si, Ge) [42] or the $CaTiO_3$ structure type (cubic, $Pm\bar{3}m$; A = Ca, Sr, Ba, Eu; X = Sn, Pb) [43, 44]. In order to create room for the relatively large planar rings of Ge_6^{10-} Zintl anions, the unique compound $Ba_{10}Ge_7O_3$ (hexagonal, *P6/mmm*) [29] exhibits a significantly different three-dimensional network than the A_3XO representatives.

Interestingly, similar confacial columns of cubes and antiprisms formed by the alkaline-earth metal component as described above (and often in other variations of the polyhedra sequence; i.e., $Ca_{31}Sn_{20}$ [45] and $Yb_{36}Sn_{23}$ [46]) can be found in the crystal structures of other Zintl phases as well. For example, the recently reported structure family $A_{16}X_{11}$ (A = Ca, Sr, Ba, Eu, Yb; X = As, Sb, Bi) [47] shows the same stacking pattern cube-antiprism-antiprism-cube as do $Ba_{11}KP_7O_2$ and $Ba_{11}KAs_7O_2$. This nicely illustrates how a variety of structures may be derived from a small set of simple cation polyhedra (octahedra, cubes and prisms) centered by oxygen and Zintl anions.

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