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Synthesis, Crystal and Electronic Structures of the Pnictides AE_3TrPn_3 (AE = Sr, Ba; Tr = Al, Ga; Pn = P, As)

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Abstract: The new ternary arsenides AE_3TrAs_3 (AE = Sr, Ba; Tr = Al, Ga) and their phosphide analogs Sr₃GaP₃ and Ba₃AlP₃ have been prepared by reactions of the respective elements at high temperatures. Single-crystal X-ray diffraction studies reveal that Sr₃AlAs₃ and Ba₃AlAs₃ adopt the Ba₃AlSb₃-type structure (Pearson symbol *oC*56, space group *Cmce*, *Z* = 8). This structure is also realized for Sr₃GaP₃ and Ba₃AlP₃. The compounds Sr₃GaAs₃ and Ba₃GaAs₃ crystallize with the Ba₃GaSb₃-type structure (Pearson symbol *oP*56, space group *Pnma*, *Z* = 8). Both structures are made up of isolated pairs of edge-shared Al*Pn*₄ and Ga*Pn*₄ tetrahedra (*Pn* = pnictogen, *i.e.*, P or As), separated by the alkaline-earth Sr²⁺ and Ba²⁺ cations. In both cases, there are no homoatomic bonds, hence, regardless of the slightly different atomic arrangements, both structures can be rationalized as valence-precise $[AE^{2+}]_3[Tr^{3+}][Pn^{3-}]_3$, or rather $[AE^{2+}]_6[Tr_2Pn6]^{12-}$, *i.e.*, as Zintl phases.

Keywords: arsenide; barium; crystal structure; phosphide; strontium; Zintl phases

1. Introduction

Our research group had previously searched for new compounds in ternary AE-Ga-Sb and AE-In-Sb phase diagrams (AE = Ca, Sr, Ba, Eu and Yb) [1–5]. Since other groups had also explored the same ternary systems and had used the traditional solid-state synthesis methods [6–12], we focused our exploratory work aimed at new compounds and structures on the metal flux method [13,14]. After

all, the triel elements Ga and In are particularly well-suited for such endeavors, and we have applied this technique to grow crystals of many new phases [1-5,15-20].

The studies on the *AE*–*Tr*–Sb ternary systems (*AE* = <u>a</u>lkaline-<u>e</u>arth metal, *i.e.*, Ca, Sr, Ba; *Tr* = <u>tr</u>iel element, *i.e.*, Al, Ga, In) proved to be fruitful [2,4,5], and subsequently, we extended our investigations toward the corresponding arsenide and phosphide systems. Published examples from our prior work on the subject include BaGa₂*Pn*₂ (*Pn* = P, As) [16], CaGa₂*Pn*₂ (*Pn* = <u>pn</u>ictogen, *i.e.*, P, As) and SrGa₂As₂ [17], *AE*₃Ga₂*Pn*₄ and *AE*₃Al₂*Pn*₄ (*AE* = Ca, Sr, Ba, Eu and Yb; *Pn* = P, As) [18], Ba₃Al₃*Pn*₅ (*Pn* = P, As, Sb) and Ba₃Ga₃Ps [19], Ba₇Ga₄*Pn*₉ (*Pn* = P, As, Sb) [20], among others.

Herein, we present the synthesis and the crystal structures of several more newly synthesized compounds— AE_3AlAs_3 for AE = Sr and Ba, and Sr₃GaP₃ and Ba₃AlP₃, all adopting the Ba₃AlSb₃-type structure [21], and AE_3GaAs_3 for AE = Sr and Ba, isostructural with the previously reported Ba₃GaSb₃ [22]. The bonding characteristics of the two structures are elaborated and the electronic structures, computed on the basis of the TB-LMTO (tight-binding linear muffin tin orbital) method [23] are also discussed.

2. Results and Discussion

2.1. Crystal Structures

The title compounds crystallize with two known structures—the Ba₃AlSb₃-type structure (Pearson symbol oC56, space group Cmce, Z = 8) [21,24], and the closely related Ba₃GaSb₃-type structure (Pearson symbol oP56, space group Pnma, Z = 8) [22,24]. A schematic representation of the two structures is given in Figure 1. Notice that there are two additional types of structures realized for some other compounds with general formulae AE_3TrPn_3 , one of which, Ca₃AlAs₃ [21], has the same global symmetry as the Ba₃GaSb₃ structure type (space group Pnma), but with fewer atoms in the unit cell (Pearson symbol oP28) and a very different atomic structure. Sr₃GaSb₃ is the only "3-1-3" phase that crystallizes in its own monoclinic structure type (Pearson symbol mP56, space group $P2_1/c$, Z = 8) [24,25]. A schematic representation of these two structures is given in Figure 2.



Figure 1. (a) Combined ball-and-stick and polyhedral representation of the crystal structure of Ba₃AlSb₃ (space group *Cmce*) and (b) Ba₃GaSb₃ (space group *Pnma*), viewed down the direction of the *b*- and *c*-axis, respectively. The blue circles represent the Ba atoms, the green circles are the Al or Ga atoms, and the red circles are the Sb atoms. The unit cells are outlined by solid black lines.



Figure 2. (a) Combined ball-and-stick and polyhedral representation of the crystal structure of Ca₃AlAs₃ (space group *Pnma*) and (b) Sr₃GaSb₃ (space group $P2_1/c$), both viewed approximately down the *b* direction. The blue circles are the Ca or Sr atoms, the green circles denote the Al or Ga atoms, and the red circles are the pnictogen atoms. The unit cells are outlined by solid black lines.

All crystal data and refinement parameters for AE_3 AlAs₃ and AE_3 GaAs₃ (AE = Sr and Ba) are summarized in Table 1. Refined atomic coordinates and distances can be found in Tables 2–5.

Sr₃AlAs₃ and Ba₃AlAs₃ are isotypic, and crystallize with the orthorhombic space group *Cmce* (No. 64, Pearson symbol *oC*56) [24]. This structure formally belongs to the Ba₃AlSb₃-type structure, which has been discussed in an earlier publication [21]. For Sr₃GaP₃ and Ba₃AlP₃, the structures were initially deduced based on the lattice parameters, and assigned to the same structure type as Sr₃AlAs₃ and Ba₃AlAs₃ (Figure 1a). To date, unequivocal refinements of the crystal structure were only possible for Ba₃AlP₃; the same could not be done for Sr₃GaP₃ due to the lack of suitable single-crystals (CIFs provided in supporting information).

The discussion below is based on Ba₃AlAs₃. The asymmetric unit of this structure contains two alkaline-earth metal atoms, and two pnictogen atoms, located at either the general site 16*g* or the special position 8*f*; the single Al atom is at 8*d* (Table 2). The Al and the As atoms constitute AlAs₄ tetrahedra, which by sharing common edges form isolated $[Al_2As_6]^{12-}$ units, isosteric with the diborane molecule B₂H₆, as shown in Figure 3. These units are oriented along the *a* axis, arranged in parallel slabs at z = 0, and $z = \frac{1}{2}$. The Ba²⁺ cations separate and counterbalance the charge of the polyanions.



Figure 3. (a) The $[Al_2As_6]^{12-}$ polyanion, isosteric with the diborane molecule, B_2H_6 ; (b) The coordination of each As and Al atoms by Barium. The blue spheres represent the Ba atoms, the green spheres denote the Al atoms, and the red ones are the arsenic atoms, respectively.

Formula	Sr3AlAs3	Ba3AlAs3	Sr3GaAs3	Ba3GaAs3
Formula weight	514.60	663.76	557.34	706.50
Space group	<i>Cmce</i> (No. 64)	<i>Cmce</i> (No. 64)	Pnma (No. 62)	Pnma (No. 62)
<i>a</i> (Å)	19.149(2)	19.854(3)	12.757(6)	13.3589(10)
<i>b</i> (Å)	6.5652(8)	6.8636(9)	19.268(9)	19.9788(15)
<i>c</i> (Å)	12.6871(15)	13.2849(17)	6.503(3)	6.8008(5)
$V(Å^3)$	1595.0(3)	1810.3(4)	1598.6(13)	1815.1(2)
Ζ	8	8	8	8
<i>T</i> (K)	200(2)	200(2)	200(2)	200(2)
$\rho_{calcd} \left(g \cdot cm^{-3}\right)$	4.29	4.87	4.63	5.17
Crystal size (m)	$30 \times 40 \times 60$	$20 \times 30 \times 50$	$30 \times 40 \times 110$	$40 \times 80 \times 135$
Radiation		Graphite-monochrom	ated Mo $K\alpha$, $\lambda = 0.71073$	Å
$\mu(Mo K\alpha) (cm^{-1})$	323.5	237.9	354.6	265.4
Transmission factors	0.260-0.424	0.414-0.648	0.112-0.397	0.116-0.395
2θ (Mo $K\alpha$) limits	4.26°-56.52°	4.10°-56.54°	4.22°-61.78°	4.08°-61.62°
	$-25 \le h \le 25,$	$-26 \le h \le 26,$	$-18 \le h \le 17,$	$-19 \le h \le 19,$
Data collected	$-8 \le k \le 8,$	$-9 \le k \le 9,$	$-27 \le k \le 27,$	$-28 \le k \le 28,$
	$-16 \le l \le 16$	$-17 \le l \le 17$	$-9 \le l \le 9$	$-9 \le l \le 9$
No. of data collected	7323	8248	16886	18478
No. of unique data,	1029	1151	2511	2830
including $F_0^2 < 0$	$(R_{\rm int} = 0.058)$	$(R_{\rm int} = 0.037)$	$(R_{\rm int} = 0.066)$	$(R_{\rm int} = 0.028)$
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	884	1031	1844	2527
No. of variables	37	37	71	71
R(F) for $F_o^2 > 2\sigma (F_o^2)^a$	0.023	0.017	0.027	0.016
$R_{ m w}(F_{ m o}{}^2)$ b	0.041	0.036	0.046	0.031
Goodness of fit	1.074	1.003	1.054	1.114
$(\Delta \rho)_{\text{max}},$ $(\Delta \rho)_{\text{min}} (e \text{ Å}^{-3})$	[0.77, -1.01]	[0.77, -1.07]	[1.28, -1.33]	[0.89, -0.82]

Table 1. Crystallographic Data for AE_3TrAs_3 (AE = Sr, Ba; Tr = Al, Ga).

^a $R(F) = \sum ||F_o| - |F_c|| \sum |F_o|$; ^b $R_w(F_o^2) = [\sum [w(F_o^2 - F_c^2)^2] / \sum w F_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2, 0) + 2F_c^2] / 3$.

Table 2. Positional and equivalent isotropic displacement parameters for AE_3AlAs_3 (AE = Sr, Ba).

Atom	Wyckoff Position	x	У	Z.	U _{eq} (Å ²) ^a
Sr ₃ AlAs ₃					
Sr1	8 <i>f</i>	0	0.17463(8)	0.34891(4)	0.0102(1)
Sr2	16g	0.17691(2)	0.31222(6)	0.13126(3)	0.0104(1)
Al	8d	0.08500(1)	0	0	0.0086(4)
As1	8 <i>f</i>	0	0.20879(9)	0.10250(5)	0.0095(1)
As2	16g	0.34135(2)	0.29606(6)	0.12022(3)	0.0095(1)

Atom	Wyckoff Position	x	У	Z	$U_{ m eq}({ m \AA}^2)$ a
Ba ₃ AlAs ₃					
Ba1	8 <i>f</i>	0	0.17015(4)	0.34685(2)	0.0116(1)
Ba2	16g	0.17563(1)	0.31318(3)	0.13014(2)	0.0116(1)
Al	8 <i>d</i>	0.08294(7)	0	0	0.0099(3)
As1	8 <i>f</i>	0	0.20319(7)	0.09613(4)	0.0109(1)
As2	16g	0.34345(2)	0.30905(5)	0.11805(3)	0.0111(1)

Table 2. Cont.

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

The Al–As distances are in the narrow range 2.507(1) Å and 2.5126(9) Å (Table 3), closely matching the sum of the corresponding Pauling's single-bond radii of Al (1.248 Å) and As (1.210 Å) [26]. These values also compare well with those reported for other ternary arsenides with similar bonding patterns, for example Na₃AlAs₂ ($d_{Al–As} = 2.507$ Å) [27], and Ca₃AlAs₃ ($d_{Al–As} = 2.503-2.540$ Å) [21], suggesting strong covalent bonding character of the Al–As interactions.

As1 and As2 atoms are both surrounded by six Ba-atoms in very distorted octahedral fashion. The Ba–As distances are in the range 3.2843(5)–3.7362(7) Å. The Al atom has 4 nearest Ba atoms in its second coordination sphere (3.3–3.4 Å away). Such distances are longer than the sum of the respective Pauling's radii ($r_{Ba} = 1.981$ Å; $r_{As} = 1.210$ Å and $r_{Al} = 1.248$ Å [26]), implying very weak directional, *i.e.*, mostly electrostatic Ba–Al and Ba–As interactions. This notion is confirmed by the electronic structure calculations.

	Sr3AlAs3	Ba3AlAs3
AE1–As1	3.1199(9)	3.2933(7)
AE1–As1	3.1342(9)	3.3386(7)
$AE1-As1 (\times 2)$	3.1652(6)	3.2843(5)
AE1–As1	3.3072(9)	3.4239(7)
AE1–As1	3.5606(9)	3.7362(7)
AE2–As2	3.1538(7)	3.3358(6)
AE2–As2	3.1742(7)	3.3668(6)
AE2–As2	3.1988(7)	3.4232(6)
AE2–As2	3.2874(7)	3.4283(6)
AE2–As2	3.4096(7)	3.4845(6)
AE2–As2	3.4744(6)	3.5962(5)
Al–As2 (\times 2)	2.472(1)	2.5126(9)
Al–As1 (\times 2)	2.494(1)	2.507(1)
AE1–Al (× 2)	3.299(1)	3.4607(7)
AE2-Al	3.174(1)	3.3161(8)

Table 3. Selected interatomic distances (Å) in AE_3AlAs_3 (AE = Sr, Ba).

Sr₃GaAs₃ and Ba₃GaAs₃ are isotypic, but crystallize with the orthorhombic space group *Pnma* (No. 62, Pearson symbol *oP*56) [24]. This structure formally belongs to the Ba₃GaSb₃-type structure, which has also been discussed in an earlier publication [22]. Notice that the Ba₃AlSb₃- and Ba₃GaSb₃-type structures are very similar, but not the same (Figure 1).

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The discussion below is based on Ba₃GaAs₃. The asymmetric unit of this structure contains four alkaline-earth metal atoms, one Al, and four pnictogen atoms, located at either the general site 8*d* or the special position 4*c* (Table 2). The Ga and the As atoms constitute GaAs₄ tetrahedra, which by sharing common edges form $[Ga_2As_6]^{12-}$ units, same as those in the Ba₃AlAs₃ structure (*vide supra*).

As shown in Figure 1b, the $[Ga_2As_6]^{12-}$ units are oriented along the *b* axis, and are arranged in slabs which are offset by $\frac{1}{4a}$. The Ga–As distances are in the narrow range 2.4855(9) Å to 2.538(1) Å (Table 5), closely matching the sum of the corresponding Pauling's single-bond radii of Ga (1.246 Å) and As (1.210 Å) [26]. Notice that the $[Ga_2As_6]^{12-}$ and $[Al_2As_6]^{12-}$ units (Figures 3 and 4) are virtually identical, with the former being slightly less symmetric (an artifact of the doubled unique As cites).



Figure 4. The $[Ga_2As_6]^{12-}$ polyanion in AE_3GaAs_3 (AE = Sr, Ba). The blue spheres represent the Sr or Ba atoms, the green spheres denote the Ga atoms, and the red ones are the arsenic atoms, respectively.

Atom	Wyckoff Position	x	У	Z	U _{eq} (Å ²) ^a
Sr3GaAs3					
Sr1	8 <i>d</i>	0.01274(4)	0.57417(2)	0.27769(6)	0.0100(1)
Sr2	8 <i>d</i>	0.26474(3)	0.07335(2)	0.30854(6)	0.0098(1)
Sr3	4c	0.26816(5)	1/4	0.68712(9)	0.0094(1)
Sr4	4 <i>c</i>	0.48050(5)	1/4	0.16924(9)	0.0097(1)
Ga	8 <i>d</i>	0.12642(4)	0.16332(3)	0.01367(7)	0.0085(1)
As1	4c	0.23468(5)	1/4	0.21000(1)	0.0090(1)
As2	4c	0.01681(5)	1/4	0.81317(9)	0.0092(1)
As3	8 <i>d</i>	0.01121(4)	0.08982(3)	0.23326(6)	0.0090(1)
As4	8 <i>d</i>	0.25889(4)	0.58990(3)	0.29433(7)	0.0092(1)
Ba3GaAs3					
Ba1	8 <i>d</i>	0.01098(1)	0.575295(8)	0.27503(2)	0.0096(1)
Ba2	8 <i>d</i>	0.26589(1)	0.074780(9)	0.31222(2)	0.0096(1)
Ba3	4c	0.26836(2)	1/4	0.68616(3)	0.0090(1)
Ba4	4c	0.47937(2)	1/4	0.16338(3)	0.0093(1)
Ga	8 <i>d</i>	0.12737(2)	0.16495(1)	0.01690(4)	0.0079(1)
As1	4c	0.22915(3)	1/4	0.20661(5)	0.0085(1)
As2	4c	0.02242(3)	1/4	0.82548(5)	0.0084(1)
As3	8 <i>d</i>	0.01687(2)	0.09121(1)	0.22609(4)	0.0092(1)
As4	8 <i>d</i>	0.26014(2)	0.59211(2)	0.30814(4)	0.0091(1)

Table 4. Positional and equivalent isotropic displacement parameters for AE_3GaAs_3 (AE = Sr, Ba).

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

	Sr3GaAs3	Ba3GaAs3		Sr3GaAs3	Ba3GaAs3
AE1–As4	3.157(2)	3.3530(4)	AE3–As2	3.310(2)	3.4195(5)
AE1–As3	3.173(2)	3.3441(4)	AE3-As1	3.427(2)	3.5780(5)
AE1-As3	3.209(2)	3.4279(4)	AE4–As1	3.147(2)	3.3556(5)
AE1–As4	3.286(2)	3.4150(4)	AE4–As2	3.171(2)	3.3740(5)
AE1–As3	3.351(2)	3.4430(4)	AE4–As3 (× 2)	3.175(2)	3.2985(4)
AE1–As2	3.460(2)	3.5846(3)	AE4–As1	3.337(2)	3.4519(5)
AE2-As4	3.148(2)	3.3353(4)	AE4–As2	3.398(2)	3.5234(5)
AE2–As3	3.172(2)	3.3789(4)	Ga–As4	2.4855(9)	2.5281(4)
AE2-As4	3.190(2)	3.4082(4)	Ga–As3	2.4911(9)	2.5245(4)
AE2–As3	3.287(2)	3.3937(4)	Ga–As1	2.515(1)	2.5299(4)
AE2-As4	3.373(2)	3.4631(4)	Ga–As2	2.538(1)	2.5589(4)
AE2-As1	3.485(2)	3.6071(3)	AE1–Ga	3.113(1)	3.2505(4)
AE3-As1	3.132(2)	3.3032(5)	AE2–Ga	3.130(1)	3.2715(3)
AE3–As2	3.172(2)	3.3948(5)	<i>AE</i> 3–Ga (× 2)	3.251(1)	3.3903(4)
<i>AE</i> 3–As4 (× 2)	3.182(2)	3.2839(4)	<i>AE</i> 4–Ga (× 2)	3.241(1)	3.3948(4)

Table 5. Selected interatomic distances (Å) in AE_3 GaAs₃ (AE = Sr, Ba).

All four As atoms are surrounded by six Ba-atoms in distorted octahedral fashion. The Ba–As distances in Ba₃GaAs₃ vary between 3.2839(4) Å and 3.6071(3) Å, which is very similar to Ba₃AlAs₃, although one might notice the slightly narrow range for the former. The Ga atom has 4 nearest Ba atoms in its second coordination sphere (distances in the 3.2505(4)—3.3948(4) Å). These metrics are the most discernable differences between the two structures and suggest that the packing of the anions is strongly influenced by the second-coordination sphere interactions, thus, the reason the Al- and the Ga-compounds for the same anions and cations are in either *Cmce* or *Pnma* space groups. Figure 5, which shows superimposed fragments of the Ba₃AlAs₃ and Ba₃GaAs₃ structures, supports this notion.



Figure 5. A projection of the Ba₃AlAs₃ structure (*Cmce* space group), shifted and overlaid on top of a projection of the Ba₃GaAs₃ structure (*Pnma* space group). Ba–Al and Ba–Ga bonds are drawn as grey cylinders to guide the eye. The blue spheres represent the Ba atoms, the green spheres denote the Al or Ga atoms, and the red ones are the arsenic atoms, respectively.

2.2. Electronic Structure

Although of different type structures, both, Ba₃AlAs₃ and Ba₃GaAs₃ are valence-precise compounds and their charge-balanced formulations $[Ba^{2+}]_3Tr^{3+}[As^{3-}]_3$ (Tr = Al, Ga) are consistent with the expectations for the direction of the electron transfer based on the relative electronegativities of the constituent elements (Pauling electronegativities of 0.9 for Ba, 1.6 for Al, 1.8 for Ga, and 2.2 for As) [26].

Band structure calculations were performed for these compounds in order to give further insight for the bonding interaction between constituent elements and to prove validity of the applied Zintl concept. The density of states (DOS) diagrams for Ba₃AlAs₃ and Ba₃GaAs₃ (Figure 6) share common features. Band gaps are noticed at the Fermi level in both diagrams indicating that these compounds would be intrinsic semiconductors. The observation of a gap between the valence and the conduction band, in both cases, is consistent with the expectation for charged-balanced formulations obtained through the application of Zintl concept [28–30]. Recall that the corresponding Al–As and Ga–As interactions were suggested to be simple 2-center-2-electron bonds, and that there are no homoatomic bonds in neither Ba₃AlAs₃ nor Ba₃GaAs₃. Therefore, following the valence rules and keeping in mind that 1/3 of the arsenic atoms are 2-bonded (the pair of As atoms accounting for the edge-shared tetrahedra), and 2/3 of the arsenic atoms are 1-bonded, the formulae of the title compounds can be readily rationalized as $(Ba^{2+})_3(4b-Tr^{1-})(2b-Pn^{1-})(1b-Pn^{2-})_2$, *i.e.*, they are classic Zintl phases (the abbreviations 1b-, 2b-, and 4b- denote 1-, 2-, and 4-bonded atoms).



Figure 6. DOS (density of states) and COHP (crystal orbital Hamilton populations) diagrams for **(a)** Ba₃AlAs₃, and **(b)** Ba₃GaAs₃. The Fermi level is set as the energy reference at 0 eV. Total DOS is shown with a black curve; partial DOS of Ba, Al or Ga, and As are represented by blue, green, and red curves, respectively. The COHP curves of the Ba–As, Al–As (or Ga–As), and Ba–Al (or Ba–Ga) interactions are shown in blue, red, and green, respectively. Since the "inverted" COHP values are plotted, the positive regions represent the bonding interactions, while the negative regions denote antibonding interactions.

The DOS diagrams for both compounds share common features. The valance band consists of several sub-bands which are located at the same energy levels for both compounds except for the Al 3s and Ga 4s states. The lowest in energy are the bands of the As 4s states which can be found in the region from -11.0 to -9 eV. The energy windows from -5.1 to -4.6 eV and from -6.0 to -5.2 eV correspond to Al 3s and Ga 4s states mixed with As 4p. The crystal orbital Hamilton population (COHP) diagrams are also projected in the same energy window (Figure 6). As seen from the plots, the strongest bonding interactions are those between the triel and pnictogen atoms, in agreement with their covalent bonding character, as discussed above. The COHP curves for the Ba–Al (or Ba–Ga) and especially for the Ba–As interactions also show appreciable *p-d* mixing, which is indicative of some degree of covalency of the bonding between the pnictogen and alkaline-earth metal, *i.e.*, the cations are more than just spectators and/or space fillers. All interactions are optimized at the Fermi level.

The calculated band gap for Ba₃AlAs₃ (0.57 eV) is smaller than the calculated one for Ba₃GaAs₃ (0.78 eV), which can be likely associated with the difference in electronegativities of Al and Ga [26]. Of course, this difference can be also attributed to the slightly different atomic arrangements.

3. Experimental Section

3.1. Synthesis

Starting materials were Ca, Sr, and Ba pieces, Al granules, Ga ingots, In shot, red P powder, As lumps, and Sb shot, all with purities greater than 99.9% and purchased from Alfa Aesar or Aldrich. All reagents and products were handled within an argon-filled glovebox with controlled oxygen and moisture level below 1 ppm. Single-crystals of the AE_3AlAs_3 (AE = Sr, Ba) compounds were prepared indvertently through use of the Al or Pb fluxes in reactions attempted to optimize the yields of the compounds from the $AE_3Tr_2Pn_4$ and $AETr_2Pn_2$ series [16,18]. Mixtures of the elements were loaded into alumina crucibles covered on the top with quartz wool and placed within fused silica tubes, which were evacuated and sealed. The tubes were heated to 960 °C at a rate of 60 °C/h, held at that temperature for 20 h (samples with Al flux) or 40 h (samples with Pb flux), cooled to 750 °C at a rate of 5 °C/h (for samples with Al flux) or to 500 °C at a rate of 30 °C/h (for samples with Pb flux). The excess of metal flux was removed at 750 °C (in samples with Al flux) or at 500 °C (in samples with Pb flux) by using a centrifuge.

Generally, the title compounds were obtained as the major phase in each reaction, with AlAs, AlSb, and some unidentified products as the most common impurity phases. We surveyed the literature and found that a number of isotypic compounds known in the related AE-Tr-Pn ternary systems (AE = Ca, Sr, Ba; Tr = Al, Ga, In; Pn = P, As, Sb, Bi). However, more than a dozen possible AE_3TrPn_3 compounds were "missing" (Table 6) and we set out to synthesize as many of them as possible. The subsequent experiments involved both reactions of stoichiometric mixtures of elements, as well as using the low melting Ga, In, Pb and Bi as fluxes. Of those experiments, only the reactions of Sr/Ba and As with Ga in place of Al, readily yielded Sr₃GaAs₃ and Ba₃GaAs₃. These two phases, however, were found to be forming with a different structure than Sr₃AlAs₃ and Ba₃AlAs₃. Of all other reactions, evidence for the existence of "3-1-3" phases was found in only two other systems, namely Sr₃GaP₃ and Ba₃AlP₃. Both adopt the Ba₃AlSb₃-type structure (Pearson symbol oC56, space group Cmce, Z = 8) with unit cell parameters a = 18.786(4) Å; b = 6.3867(12) Å; c = 12.403(2) Å for Sr₃GaP₃, and

a = 19.3572(14) Å; b = 6.7433(5) Å; c = 12.9707(10) Å for Ba₃AlP₃, respectively. The efforts to synthesize any of the other compounds have been unsuccessful so far, resulting in known binary and ternary compounds.

Table 6. The known and unknown (up to date) AE_3TrPn_3 compounds (AE = Ca, Sr, Ba; Tr = AI, Ga, In; Pn = P, As, Sb, Bi) ^a. Four distinct structure can be distinguished— Ca₃AlAs₃ structure type (Pearson symbol oP28, space group Pnma, Z = 4; a = 12.212 Å, b = 4.201 Å, c = 13.434 Å), shaded in blue; Ba₃GaSb₃ structure type (Pearson symbol oP56, space group Pnma, Z = 8; a = 14.117 Å, b = 21.167 Å, c = 7.128 Å) shaded in pink; Ba₃AlSb₃ structure type (Pearson symbol oC56, space group Cmce, Z = 8; a = 21.133 Å, b = 7.194 Å, c = 14.069 Å) shaded in green; and the Sr₃GaSb₃ structure type (Pearson symbol mP56, space group $P2_1/c$, Z = 8; a = 11.749 Å, b = 14.509 Å, c = 13.485 Å, $\beta = 124.955^{\circ}$).

AE Tr	Са	Sr	Ва	AE Pn
	—	—	Ba ₃ AlP ₃ [this work]	Р
Al	Ca ₃ AlAs ₃ [21]	Sr3AlAs3 [this work]	Ba3AlAs3 [this work]	As
	Ca ₃ AlSb ₃ [31]	Sr ₃ AlSb ₃ [32]	Ba3AlSb3 [21]	Sb
	—	Sr ₃ GaP ₃ [this work]	Ba3GaP3 [33]	Р
Ga	Ca ₃ GaAs ₃ [22]	Sr ₃ GaAs ₃ [this work]	Ba ₃ GaAs ₃ [this work]	As
	—	Sr3GaSb3 [25]	Ba3GaSb3 [22]	Sb
	Ca ₃ InP ₃ [22]	Sr ₃ InP ₃ [25]	—	Р
In	_	_	Ba ₃ InAs ₃ [34]	As
	_	_	_	Sb

^a Bismuthides with these structures are not known.

3.2. X-ray Diffraction

Suitable single crystals were selected under an optical microscope in the glovebox, mounted on glass fibers using Paratone oil, and placed immediately under a cold nitrogen gas stream on a Bruker SMART CCD-based diffractometer equipped with a Mo K α radiation source. Full spheres of intensity data were collected at -73 °C using ω scans with a scan width of 0.4° and an exposure time of 12 s per frame in 4 batches [35]. Semi-empirical absorption corrections based on the equivalent reflections were applied using SADABS [36]. Structure solution and refinement were carried out with the use of SHELXTL program package [37]. The centrosymmetric space groups *Cmce* (No. 64) and *Pnma* (No. 62) were chosen based on the Laue symmetry, systematic absences and intensity statistics for *AE*₃AlAs₃ and *AE*₃GaAs₃, respectively. Direct methods yielded structural models consistent with the Ba₃AlSb₃-(for Al compounds) and Ba₃GaSb₃-type structures (for Ga compounds) and further refinements proceeded without any complications. The crystal quality for Sr₃GaP₃ was inadequate, but based on the unit cell parameters (*vide supra*) and the base-centering conditions of the observed reflections, we can argue that this phosphide, as well as Ba₃AlP₃, both crystallize with the Ba₃AlSb₃-type structure (Pearson symbol *oC*56, space group *Cmce*, *Z* = 8).

Crystal data are given in Table 1. Atom coordinates were standardized with the program STRUCTURE TIDY [38]. Atom labels are left the same, as they appear in the prototype compounds for easy comparison. Final values of the atomic positional and equivalent displacement parameters are given in Tables 2 and 4. Selected interatomic distances are listed in Tables 3 and 5. Additional information in the form of crystallographic information files (CIFs), is available as Supporting Information or may be obtained from Fachinformationszentrum Karlsruhe, Abt. PROKA, 76344 Eggenstein-Leopoldshafen, Germany (No. CSD-430165 to 430169).

3.3. Electronic Structure Calculations

Tight-binding linear muffin tin orbital [23] band structure calculations were performed on Ba₃AlAs₃ and Ba₃GaAs₃ within the local density and atomic spheres approximation with use of the Stuttgart TB-LMTO-ASA program (version 4.7). The basis sets included Ba 6s/6p/5d/4f, Al 3s/3p/3d, Ga 4s/4p/4d, and As 4s/4p/4d orbitals, with the Ba 6p, Al 3d, Ga 4d, and As 4d orbitals being downfolded. Integration in reciprocal space were carried out with an improved tetrahedron method over 172 (Ba₃AlAs₃) and 112 (Ba₃GaAs₃) irreducible k points within the first Brillouin zone.

4. Conclusions

With this article, we reported on the synthesis and the structural characterization of the new ternary arsenides: AE_3AlAs_3 and AE_3GaAs_3 (AE = Sr and Ba) and the phosphides Sr_3GaP_3 and Ba_3AlP_3. Attempts to synthesize other possible, but hitherto unknown compounds with the chemical formulae AE_3TrPn_3 (AE = Ca, Sr, Ba; Tr = Al, Ga, In; Pn = P, As, Sb, Bi) were not successful. Sr_3AlAs_3 and Ba_3AlAs_3 are isotypic, and crystallize with the orthorhombic space group Cmce (No. 64, Pearson symbol oC56). Sr_3GaAs_3 and Ba_3GaAs_3 are isotypic, and crystallize with the orthorhombic space group Pnma (No. 62, Pearson symbol oP56). All are "normal" Zintl phases (*i.e.*, small band semiconductors), and some interesting charge/heat transport properties could be expected. The high air-and moisture-sensitivity of the crystalline materials, however, are problematic and preclude property measurements.

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Author Contributions

Stanislav S. Stoyko, Leonard H. Voss, and Hua He contributed to obtaining the experimental results detailed in this paper. Stanislav S. Stoyko was the lead person for the electronic structure calculations. The project was supervised, and the paper was written by Svilen Bobev.

Conflicts of Interest

The authors declare no conflict of interest.

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