Synthesis and Structural Characterization of the Zintl Phases $\text{Na}_3\text{Ca}_3\text{TrPn}_4$, $\text{Na}_3\text{Sr}_3\text{TrPn}_4$, and $\text{Na}_3\text{Eu}_3\text{TrPn}_4$ ($\text{Tr} = \text{Al, Ga, In}$; $\text{Pn} = \text{P, As, Sb}$)

Yi Wang,¹ Nian-Tzu Suen,^{1,2} Thabiso Kunene,¹ Stanislav Stoyko,¹ and Svilen Bobev¹

¹ Department of Chemistry & Biochemistry, University of Delaware, 304A Drake Hall, Newark, DE 19716

² College of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, P.R. China

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Abstract

15 new quaternary Zintl phases have been synthesized by solid-state reactions from the respective elements, and their structures have been determined by single-crystal X-ray diffraction. $\text{Na}_3\text{E}_3\text{TrPn}_4$ ($\text{E} = \text{Ca, Sr, Eu}$; $\text{Tr} = \text{Al, Ga, In}$; $\text{Pn} = \text{P, As, Sb}$) crystallize in the hexagonal crystal system with the non-centrosymmetric space group $P6_3mc$ (No. 186). The structure represents a variant of the K_6HgS_4 structure type (Pearson index $hP22$) and features $[\text{TrPn}_4]^{9-}$ tetrahedral units, surrounded by Na^+ and Ca^{2+} , Sr^{2+} , Eu^{2+} cations. The nominal formula rationalization $[\text{Na}^+]_3[\text{E}^{2+}]_3[\text{TrPn}_4]^{9-}$ follows the octet rule, suggesting closed-shell configurations for all atoms and intrinsic semiconducting behavior. However, structure refinements for several members hint at disorder and mixing of cations that potentially counteract the optimal valence electron count.

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1. Introduction

In recent years, there has been a growing interest in several kinds of ternary antimonides as prospective materials for applications in thermoelectric energy conversion [1–6]. These materials can be generally classified as Zintl phases [7,8], i.e., solids based on metals and semi-metals, in which the structures can be rationalized as cations (less electronegative elements) and anions (more electronegative elements), so that the valence rules are satisfied. Our research group has been very active in this field, and in the last three years alone [9–13], we have reported on more than a dozen new Zintl phases based on the alkali- or alkaline-earth metals and the post-transition elements from groups 13–15. Ongoing research efforts are focused on the properties of several classes of newly synthesized materials, and expanding the knowledge in this general area by systematic exploratory work in related ternary and quaternary systems.

* Corresponding author. Tel.: +1-302-831-8720; fax: +1-302-831-6335.

E-mail address: bobev@udel.edu.

Specifically, in one of our most recent publications, we described three new Zintl phases— $\text{Na}_{11}\text{Ca}_2\text{Al}_3\text{Sb}_8$, $\text{Na}_4\text{CaGaSb}_3$, and $\text{Na}_{15}\text{Ca}_3\text{In}_5\text{Sb}_{12}$ [11]. Their complex structures contain Na^+ and Ca^{2+} cations and the following polyanions— $[\text{Al}_3\text{Sb}_8]$ isolated units made of three AlSb_4 tetrahedra; one-dimensional $[\text{GaSb}_3]$ helical chains of corner-shared GaSb_4 tetrahedra; and $[\text{In}_5\text{Sb}_{12}]$ layers, made of corner-shared InSb_4 tetrahedra, respectively. In all three examples mentioned above, a significant contribution of the Na^+ and Ca^{2+} cations to the chemical bonding was noted, which motivated us to extend our research and to seek more new structures with intricate bonding characteristics. In ref. #11, we also mentioned that other quaternary phosphide-, arsenide-, and antimonide-based compounds were identified as side products of the reactions and that work to identify them has been ongoing.

In this paper, we report on a large family of compounds spanning 15 members— $\text{Na}_3\text{Ca}_3\text{TrPn}_4$, $\text{Na}_3\text{Sr}_3\text{TrPn}_4$, and $\text{Na}_3\text{Eu}_3\text{TrPn}_4$ ($\text{Tr} = \text{Al, Ga, In}$; $\text{Pn} = \text{P, As, Sb}$). These join the isotypic $\text{Na}_3\text{Ca}_3\text{AlAs}_4$ [14], and $\text{Na}_3\text{Ca}_3\text{GaPn}_4$ ($\text{Pn} = \text{P, As, Sb}$) [15], which have been reported more than 2 decades ago by von Schnering *et al.* The emphasis of this study is on the synthesis and the structural characterization of these (presumed) Zintl phases. Specific attention is paid to the structure refinements for several members, which are suggestive of occupational and/or positional disorder that potentially negates the optimal valence electron count. The associated off-stoichiometry calls into question the simplistic description of the chemical bonding that follows the Zintl-Klemm concept [7,8].

2. Experimental Methods

2.1. Synthesis

Due to the high sensitivity of some of the elements to air and moisture, Na metal in particular, handling of the reactants required extreme caution. All manipulations were carried out inside an argon-field glove-box with controlled atmosphere or under vacuum. The metals were purchased from Alfa or Aldrich (purity >99.9%), and were used as received. The alkali and alkaline-earth metals' surface was scrapped off with a scalpel blade immediately before use. The starting materials were weighed in the glove-box, loaded into Nb tubes, which were then closed by arc-welding under high purity argon gas. The sealed Nb containers were subsequently jacketed within evacuated fused silica tubes. The reaction mixtures were heated in muffle furnaces to 1173 K at a rate of 100 K/h, and equilibrated at this temperature for 24 hours. After that, the samples were cooled to 773 K at a rate of 5 K/h, at which point the cooling rate to room temperature was changed to 40 K/h.

The first structure that was identified by single-crystal X-ray diffraction methods was that of $\text{Na}_3\text{Ca}_3\text{AlSb}_4$. This phase was one of the products of an exploratory reaction that also produced $\text{Na}_{11}\text{Ca}_2\text{Al}_3\text{Sb}_8$ [11]. Several other isotypic compounds were identified from similar exploratory reactions of the respective elements. After the structures and the chemical compositions of these compounds were established, it became clear that many more $\text{A}_3\text{E}_3\text{TrPn}_4$ ($\text{A} = \text{Na, K}$; $\text{E} = \text{Ca, Sr, Ba, Eu, Yb}$; $\text{Tr} = \text{Al, Ga, In}$; $\text{Pn} = \text{P, As, Sb}$) phases could exist, and the missing members were targeted in more than 40 additional reactions. The latter experiments produced almost a dozen of the sought after quaternary phases. In nearly all systems, there were multiple products identified from the powder X-ray diffraction patterns of the as-synthesized materials. The extreme air-sensitivity of the samples severely hindered the structural characterization, and the identity of many of the products is still unknown.

Caution! At the aforementioned conditions, Na and K metals will evaporate. It is therefore important to use as long as possible Nb-containers, and long fused silica tubes, which must be left protruding outside the furnace. Doing so minimizes the risk of serious accidents since in case of a leak, the alkali metal vapors (under certain pressure) will diffuse and condense at the cold end of the fused silica tube. If this happens the furnace must be stopped immediately.

2.2. Powder X-Ray Diffraction

The as-synthesized samples were ground in the glove-box to fine powders. Then, powder X-ray diffraction patterns were taken at room temperature on a Rigaku MiniFlex powder diffractometer, also operated inside the

glove-box. The tabletop diffractometer uses filtered Cu K α radiation ($\lambda = 1.541 \text{ \AA}$, the weighted-mean wavelength of the K α_1 and K α_2 components), therefore, the recorded powder X-ray diffraction patterns could only be used for basic phase identification. Data analysis was done using the JADE 6.5 software package.

2.3. Single-crystal X-Ray Diffraction

Single-crystal X-ray diffraction data were obtained on a Bruker APEX II CCD-based diffractometer with a 3-circle goniometer and employing monochromatized Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). An inert atmosphere was maintained by nitrogen gas flow. The temperature was kept at 200 K throughout the whole experiment.

For each crystal, nearly a full sphere of reciprocal data were gathered with frame width 0.4° in ω and θ , and 10 s exposure time per frame. Data acquisition and integration were completed using the APEX-suite of programs, supplied by Bruker [16]. Semi-empirical absorption correction based on equivalent reflections was applied using SADABS [17]. The structures were solved by direct methods and refined with the full-matrix least squares method on F^2 , as implemented in SHELX [18]. Parameters in the refinements included the scale factors, the atomic positions, and the occupation factors for the split and mixed-occupied sites. Where applicable, extinction coefficients were also refined. In nearly all cases, the absolute structures were established, as evidenced by the refined Flack parameters [19].

Further details of the structural work are discussed later on in the context of the structural description. Here, we just mention that occupational disorder was found in almost all structures. For simplicity, however, the formulae are referred to as $\text{Na}_3\text{E}_3\text{TrPn}_4$ ($\text{E} = \text{Ca, Sr, Eu; Tr} = \text{Al, Ga, In; Pn} = \text{P, As, Sb}$) instead of the refined off-stoichiometric $\text{Na}_{3+x}\text{E}_{3-x}\text{TrPn}_4$ ($0 < x < 0.6$).

Table 1

Selected single-crystal data collection and structure refinement parameters for $\text{Na}_3\text{E}_3\text{TrPn}_4$ ($\text{E} = \text{Ca, Eu, Sr; Tr} = \text{Al, Ga, In}$).

Empirical formula	$\text{Na}_3\text{Ca}_3\text{AlP}_4$	$\text{Na}_3\text{Ca}_3\text{GaP}_4$	$\text{Na}_3\text{Ca}_3\text{InP}_4$	$\text{Na}_{3.12(1)}\text{Eu}_{2.88}\text{AlP}_4$	$\text{Na}_{3.40(4)}\text{Eu}_{2.60}\text{InP}_4$	$\text{Na}_{3.26(2)}\text{Sr}_{2.74}\text{InP}_4$
Formula weight	340.07	382.81	427.91	660.23	711.96	554.37
Space group	$P6_3mc$ (No. 186), $Z = 2$					
Radiation	Mo K α , $\lambda = 0.71073 \text{ \AA}$					
Temperature	-73°C					
Unit cell parameters						
$a / \text{\AA}$	9.1655(9)	9.174(2)	9.3580(3)	9.3222(4)	9.4959(12)	9.5114(8)
$c / \text{\AA}$	7.0266(13)	7.035(4)	7.1477(5)	7.2880(6)	7.3505(18)	7.4365(12)
$V / \text{\AA}^3$	511.20(12)	512.8(3)	542.08(5)	548.50(6)	574.01(17)	582.62(12)
c/a	0.767	0.767	0.764	0.782	0.774	0.782
$\rho_{\text{calc}} / \text{g cm}^{-3}$	2.21	2.48	2.62	4.00	4.12	3.16
μ / cm^{-1}	23.8	48.6	42.4	169.9	166.2	150.9
Data : parameters ratio	559 : 27	557 : 27	592 : 26	595 : 27	628 : 27	639 : 27
Flack parameter	0.15(13)	0.00(4)	0.04(7)	0.01(1)	0.06(6)	0.01(2)
Final $R1^a$ ($I > 2\sigma_I$)	$R1 = 0.043$ $wR2 = 0.083$	$R1 = 0.050$ $wR2 = 0.084$	$R1 = 0.026$ $wR2 = 0.079$	$R1 = 0.009$ $wR2 = 0.021$	$R1 = 0.053$ $wR2 = 0.129$	$R1 = 0.037$ $wR2 = 0.089$
Goodness of fit	1.054	1.078	1.188	1.080	1.147	1.097
Largest diff. peak & hole / $\text{e}^- \text{\AA}^{-3}$	0.72 & -0.66	1.06 & -0.58	0.91 & -0.73	0.32 & -0.43	2.57 & -1.98	1.51 & -0.75

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$, where $w = 1 / [\sigma^2(F_o^2) + (A \cdot P)^2 + (B \cdot P)]$, and $P = (F_o^2 + 2F_c^2) / 3$. A and B are weight coefficients, respectively. Please refer to the CIFs, provided as electronic supporting information.

Selected crystallographic information and refinement parameters for $\text{Na}_3\text{E}_3\text{TrP}_4$, $\text{Na}_3\text{E}_3\text{TrAs}_4$, and $\text{Na}_3\text{E}_3\text{TrSb}_4$ ($\text{E} = \text{Ca}, \text{Sr}, \text{Eu}$; $\text{Tr} = \text{Al}, \text{Ga}, \text{In}$) are summarized in Tables 1, 2, and 3, respectively. $\text{Na}_3\text{Sr}_3\text{InP}_4$, $\text{Na}_3\text{Sr}_3\text{InAs}_4$, and $\text{Na}_3\text{Sr}_3\text{InSb}_4$ were chosen as representatives of the phosphides, arsenides, and antimonides and final positional and equivalent isotropic displacement parameters for each are given in Table 4. Relevant interatomic distances and angles for the same three compounds are listed in Table 5. Table 6 provides side-by-side comparison of important structural data from the refinements of $\text{Na}_{3.41(1)}\text{Eu}_{2.59}\text{AlSb}_4$ and $\text{Na}_3\text{Eu}_3\text{AlSb}_4$, a case which best exemplifies the differences between the models with and without disorder. All CIFs are provided as supporting information; the files have also been deposited with Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: (49) 7247-808-666; e-mail: crysdata@fiz.karlsruhe.de) with depository numbers: CSD-432471 for $\text{Na}_3\text{Ca}_3\text{AlP}_4$, CSD-432472 for $\text{Na}_3\text{Ca}_3\text{GaP}_4$, CSD-432470 for $\text{Na}_3\text{Ca}_3\text{InP}_4$, CSD-432473 for $\text{Na}_3\text{Eu}_3\text{AlP}_4$, CSD-432474 for $\text{Na}_3\text{Eu}_3\text{InP}_4$, CSD-432475 for $\text{Na}_3\text{Sr}_3\text{InP}_4$, CSD-432476 for $\text{Na}_3\text{Ca}_3\text{GaAs}_4$, CSD-432477 for $\text{Na}_3\text{Eu}_3\text{AlAs}_4$, CSD-432478 for $\text{Na}_3\text{Eu}_3\text{GaAs}_4$, CSD-432479 for $\text{Na}_3\text{Sr}_3\text{InAs}_4$, CSD-432480 for $\text{Na}_3\text{Ca}_3\text{AlSb}_4$, CSD-432481 for $\text{Na}_3\text{Eu}_3\text{AlSb}_4$, CSD-432482 for $\text{Na}_3\text{Eu}_3\text{GaSb}_4$, CSD-432484 for $\text{Na}_3\text{Sr}_3\text{AlSb}_4$, and CSD-432483 for $\text{Na}_3\text{Sr}_3\text{InSb}_4$.

Table 2

Selected single-crystal data collection and structure refinement parameters for $\text{Na}_3\text{E}_3\text{TrAs}_4$ ($\text{E} = \text{Ca}, \text{Eu}, \text{Sr}$; $\text{Tr} = \text{Al}, \text{In}$).

Empirical formula	$\text{Na}_{3.14(4)}\text{Ca}_{2.86}\text{GaAs}_4$	$\text{Na}_{3.10(2)}\text{Eu}_{2.90}\text{AlAs}_4$	$\text{Na}_{3.10(2)}\text{Eu}_{2.90}\text{GaAs}_4$	$\text{Na}_{3.34(2)}\text{Sr}_{2.66}\text{InAs}_4$
Formula weight	556.05	838.61	881.35	724.36
Space group	$P6_3mc$ (No. 186), $Z = 2$			
Radiation	Mo $K\alpha$, $\lambda = 0.71073 \text{ \AA}$			
Temperature	-73°C			
Unit cell parameters				
$a / \text{\AA}$	9.4069(9)	9.5621(7)	9.5566(12)	9.7426(12)
$c / \text{\AA}$	7.2039(14)	7.4418(11)	7.4319(19)	7.605(2)
$V / \text{\AA}^3$	552.07(13)	589.27(11)	587.81(18)	625.1(2)
c/a	0.766	0.778	0.778	0.780
$\rho_{\text{calc}} / \text{g cm}^{-3}$	3.35	4.73	4.98	3.85
μ / cm^{-1}	157.7	265.42	287.5	236.8
Data : parameters ratio	595 : 28	645 : 28	647 : 27	687 : 27
Flack parameter	0.01(3)	0.01(6)	0.1(1)	0.01(3)
Final $R1^a$ ($I > 2\sigma_I$)	$R1 = 0.031$ $wR2 = 0.051$	$R1 = 0.030$ $wR2 = 0.049$	$R1 = 0.033$ $wR2 = 0.069$	$R1 = 0.036$ $wR2 = 0.075$
Goodness of fit	1.100	1.060	1.072	1.064
Largest diff. peak & hole $/e^- \text{\AA}^{-3}$	0.89 & -0.78	1.26 & -1.24	1.44 & -1.17	0.89 & -1.18

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2 F_o^2 + (A \cdot P)^2 + (B \cdot P)]$, and $P = (F_o^2 + 2F_c^2)/3$. A and B are weight coefficients, respectively. Please refer to the CIFs, provided as electronic supporting information.

2.4. Electronic Structure Calculations

The electronic structures of $\text{Na}_3\text{Ca}_3\text{AlP}_4$, $\text{Na}_3\text{Ca}_3\text{GaP}_4$, $\text{Na}_3\text{Ca}_3\text{InP}_4$, $\text{Na}_3\text{Sr}_3\text{InP}_4$, $\text{Na}_3\text{Sr}_3\text{InAs}_4$ and $\text{Na}_3\text{Sr}_3\text{InSb}_4$ were computed. The calculations were carried out with the linear muffin-tin orbital (TB-LMTO) method [20] using the Stuttgart TB-LMTO-4.7 program [21]. The total and partial Density of States (DOS) and the Crystal Orbital Hamilton Populations (COHP) curves of selected interactions are presented and discussed. Exchange and correlation terms were treated by the local density approximation (LDA) approach [22]. In addition, the scalar

relativistic approximation was employed to treat all relativistic effects, except for spin-orbit coupling [23]. Spherical potential well is considered in each Wigner-Seitz (WS) sphere, and the corresponding values were determined by the default settings [24]. The radii of the WS spheres for each element are as follow: Na = 1.73–1.84 Å; Sr = 2.11–2.24 Å; In = 1.53–1.63 Å; P = 1.45–1.51 Å; As = 1.54–1.62 Å, and Sb = 1.71–1.79 Å. The basis sets contained 3s, 3p and 3d orbitals for Na; 5s, 5p, and 4d orbitals for Sr; 5s, 5p and 5d orbitals for In; 3s, 3p and 3d orbitals for P; 4s, 4p and 4d orbitals for As; 5s, 5p and 5d orbitals for Sb. The Löwdin downfolding technique was used to handle the high-energy vacant orbitals. There are a total of 152 irreducible k -points in the Brillouin zone in each calculation; the tetrahedron method [25] was applied to handle k -space integrations.

Table 3

Selected single-crystal data collection and structure refinement parameters for $\text{Na}_3E_3\text{TrSb}_4$ ($E = \text{Ca, Eu, Sr}$; $\text{Tr} = \text{Al, Ga, In}$).

Empirical formula	Na _{3.40(5)} Ca _{2.60} AlSb ₄	Na _{3.41(1)} Eu _{2.59} AlSb ₄	Na _{3.59(1)} Eu _{2.41} GaSb ₄	Na _{3.18(1)} Sr _{2.82} AlSb ₄	Na _{3.45(3)} Sr _{2.55} InSb ₄
Formula weight	696.35	984.66	1006.77	834.50	904.57
Space group	<i>P</i> 6 ₃ <i>mc</i> (No. 186), <i>Z</i> = 2				
Radiation	Mo Kα, λ = 0.71073 Å				
Temperature	−73°C				
Unit cell parameters					
<i>a</i> / Å	10.0121(5)	10.1272(5)	10.1138(4)	10.1587(10)	10.2610(14)
<i>c</i> / Å	7.6045(8)	7.8453(8)	7.8049(6)	7.9509(15)	7.995(2)
<i>V</i> / Å ³	660.16(8)	696.82(9)	691.40(7)	710.60(17)	729.0(3)
<i>c/a</i>	0.760	0.775	0.772	0.783	0.779
ρ _{calc} / g cm ^{−3}	3.50	4.69	4.84	3.90	4.12
μ / cm ^{−1}	92.3	191.8	204.7	181.2	181.5
Data : parameters ratio	722 : 27	749 : 28	749 : 27	768 : 28	790 : 28
Flack parameter	0.00(9)	0.01(2)	0.02(3)	0.003(9)	0.00(3)
Final R1 ^a (<i>I</i> > 2σ _{<i>I</i>})	R1 = 0.030 wR2 = 0.050	R1 = 0.016 wR2 = 0.040	R1 = 0.025 wR2 = 0.050	R1 = 0.014 wR2 = 0.033	R1 = 0.041 wR2 = 0.081
Goodness of fit	0.908	1.116	1.115	1.099	1.067
Largest diff. peak & hole / e [−] Å ^{−3}	0.93 & −0.93	0.69 & −0.91	1.22 & −1.44	0.54 & −0.87	1.61 & −1.07

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum (w(F_o^2)^2)]^{1/2}$, where $w = 1/[\sigma^2 F_o^2 + (A \cdot P)^2 + (B \cdot P)]$, and $P = (F_o^2 + 2F_c^2)/3$. A and B are weight coefficients, respectively. Please refer to the CIFs, provided as electronic supporting information.

3. Results

3.1. Synthesis

To this end, the Na-Ca- Tr-Pn , Na-Sr- Tr-Pn , and Na-Eu- Tr-Pn ($\text{Tr} = \text{Al, Ga, In}$; $\text{Pn} = \text{P, As, Sb}$) systems have proven to be a fertile ground for new materials discovery. Besides the large number of compounds described in this paper, we have already identified the quaternary phases $\text{Na}_{11}\text{Ca}_2\text{Al}_3\text{Sb}_8$, $\text{Na}_4\text{CaGaSb}_3$, and $\text{Na}_{15}\text{Ca}_3\text{In}_5\text{Sb}_{12}$ [11]. Several other compounds from these exploratory reactions await their full structural characterization.

Based on the experiments done so far, the related $\text{K}_3\text{Ca}_3\text{TrPn}_4$, $\text{K}_3\text{Sr}_3\text{TrPn}_4$, $\text{K}_3\text{Eu}_3\text{TrPn}_4$, and especially the $\text{K}_3\text{Ba}_3\text{TrPn}_4$ ($\text{Tr} = \text{Al, Ga, In}$; $\text{Pn} = \text{P, As, Sb}$) systems also seem promising. The products of the reactions containing K or Ba are extremely reactive/unstable and could not be reliably characterized. Preliminary crystallographic work is suggestive of rich chemistry and very complex structures. Although no isostructural bismuthides were found from any reaction carried out to date, we speculate that such compounds could still be

found if the reaction conditions are optimized. Another important consideration in that regard is the large size of the Bi anions—we speculate that the expected increase of the unit cell volume must be commensurate with an increase of the sizes of the cations as well. Following this conjecture, we can argue that $K_3Ba_3TrBi_4$ is a better target system for the discovery of bismuthides than $Na_3Ca_3TrBi_4$ or $Na_3Sr_3TrBi_4$.

We also need to bring attention to the general experimental difficulties encountered during the synthesis of the title compounds. Specifically, the issue of working in sealed Nb-containers. This is a requirement that comes about as a result of the low melting and boiling points of the alkali metals, coupled with their reactivity. However, the use of Nb-containers creates a complication, as the pnictogen elements, P and As in particular, have a tendency to react with Nb. The problem is exacerbated by the fact that isostructural compounds such as Na_5SrNbP_4 and $Na_5SrNbAs_4$ are known, and form at similar conditions [26, 27]. Furthermore, there are also precedents in the literature for the inadvertent Nb incorporation in related compounds, for example, the von Schnering group that spearheaded the early efforts in this area, has published the structure of $Na_{3.12}Sr_{2.88}Al_{0.94}Nb_{0.06}P_4$ [28], where a small amount of Nb is found to substitute Al. The source of Nb is the reaction container, and it has been suggested that to circumvent the facile side-reaction between Nb and P, the synthesis should be carried out using binary phosphides as starting materials.

Table 4

Atomic Coordinates and Equivalent Isotropic Displacement Parameters (U_{eq}^a) for $Na_3Sr_3InP_4$, $Na_3Sr_3InAs_4$, and $Na_3Sr_3InSb_4$.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}/\text{\AA}^2$
$Na_3Sr_3InP_4$					
Na	6c	0.8619(4)	$\bar{x}$	0.9380(8)	0.050(1)
<i>E</i> ^b	6c	0.47612(5)	$\bar{x}$	0.7743(2)	0.0267(3)
In	2b	2/3	1/3	0.6479(1)	0.0225(3)
P1	6c	0.8154(2)	$\bar{x}$	0.5439(3)	0.0228(5)
P2	2b	2/3	1/3	0.0000(5)	0.0232(8)
$Na_3Sr_3InAs_4$					
Na(A) ^c	6c	0.864(2)	$\bar{x}$	0.932(2)	0.046(2)
Na(B) ^c	6c	0.844(6)	$\bar{x}$	0.950(7)	0.046(2)
<i>E</i> ^b	6c	0.47704(7)	$\bar{x}$	0.7726(2)	0.0292(4)
In	2b	2/3	1/3	0.6439(2)	0.0278(4)
As1	6c	0.81665(8)	$\bar{x}$	0.5418(2)	0.0274(3)
As2	2b	2/3	2/3	0.0000(2)	0.0265(5)
$Na_3Sr_3InSb_4$					
Na(A) ^c	6c	0.1489(8)	$\bar{x}$	0.065(2)	0.046(3)
Na(B) ^c	6c	0.157(2)	$\bar{x}$	0.898(4)	0.046(3)
<i>E</i> ^b	6c	0.51857(9)	$\bar{x}$	0.2270(3)	0.0342(6)
In	2b	1/3	2/3	0.3628(2)	0.0249(5)
Sb1	6c	0.18091(6)	$\bar{x}$	0.4662(1)	0.0277(3)
Sb2	2b	1/3	2/3	0.0000(2)	0.0248(4)

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

^b For $Na_3Sr_3InP_4$, *E* is refined as a statistical mixture of Sr : Na = 0.913(8) : 0.087; $Na_3Sr_3InAs_4$, *E* is refined as a statistical mixture of Sr : Na = 0.886(6) : 0.114; $Na_3Sr_3InSb_4$, *E* is refined as a statistical mixture of Sr : Na = 0.851(8) : 0.149.

^c For $Na_3Sr_3InAs_4$, Na(A) and Na(B) represent a split position refined with site occupancies 0.8(1) and 0.2(1), respectively. For $Na_3Sr_3InSb_4$, Na(A) and Na(B) represent a split position refined with site occupancies 0.7(2) and 0.3(2), respectively.

We explored this strategy, but found that the use of pre-reacted Na-P and Sr-P binaries complicates, and unnecessarily prolongs the experiments. Use of precursors did not appear to improve the yields of the desired phases—considerable amounts of impurity phases, as well as leftover precursor materials outweigh the potential benefits of pursuing this route. Instead, our own experiments suggest that the unwanted Nb-P reaction can be avoided if the reactions are ran for shorter times—24 hours vs 72 hours—regardless whether the starting materials are the pure elements or in the form of precursors. The structure refinements for materials obtained by this shortened heating show no discernable Nb-content. In all of our structures, particularly those with Al and Ga (much lighter elements than Nb and therefore, easily distinguishable from their X-ray scattering forms), there are no problems with the final difference Fourier maps, which are generally flat. The corresponding anisotropic displacement parameters for Al, Ga, and In are consistent, which coupled with model refinements that show stable site occupation factors, when freed, rule out possible Nb-contamination. However, the shorter homogenization time might have an implication on the lack of full ordering on the cation sites in certain cases, which is discussed in the next section.

Fig. 1. Polyhedral views of the structure of $\text{Na}_3\text{Ca}_3\text{TrPn}_4$, $\text{Na}_3\text{Sr}_3\text{TrPn}_4$, and $\text{Na}_3\text{Eu}_3\text{TrPn}_4$ ($\text{Tr} = \text{Al, Ga, In}$; $\text{Pn} = \text{P, As, Sb}$). The packing of *Tr* (yellow) and Na (red) tetrahedra is shown in panel a). The Ca-, Sr-, or Eu-centered octahedra are drawn in green, and their packing is shown in panel b). The *Pn* atoms at the corners of the polyhedra are shown in blue, and form an *hcp* array with the *Tr* and Na atoms in $\frac{1}{2}$ of the tetrahedral holes (in an ordered fashion), and the Ca, Sr, or Eu atoms in $\frac{1}{4}$ of the available octahedral holes. The empty octahedral holes are represented with the open circles.

3.2. Crystal structure and chemical bonding

$\text{Na}_3\text{E}_3\text{TrPn}_4$ ($E = \text{Ca, Sr, Eu}$; $\text{Tr} = \text{Al, Ga, In}$; $\text{Pn} = \text{P, As, Sb}$) crystallize in the hexagonal crystal system with the non-centrosymmetric space group $P6_3mc$ (No. 186). This structure has the Pearson index $hP22$ with 5 atomic positions in the asymmetric unit (Table 4), and a Wyckoff sequence c^3b^2 . This relatively simple arrangement is adopted by many oxides and sulfides of the families of Na_6ZnO_4 and K_6HgS_4 . More than a dozen phosphides, arsenides and antimonides with general formulae $\text{Na}_4\text{E}_2\text{TiPn}_4$ and $\text{K}_4\text{E}_2\text{TiPn}_4$ ($E = \text{Ca, Sr, Ba, Eu}$; $\text{Ti} = \text{Si, Ge, Sn}$; $\text{Pn} = \text{P, As, Sb}$) have also been known for some time [29, 30]. von Schnering et al. [26] have already discussed the relationship between this and the wurtzite-type structure, which becomes apparent when one realizes that the pnictogen atoms form a hexagonal closed-packed (*hcp*) array with the *Tr* and Na atoms in $\frac{1}{2}$ of the tetrahedral holes (in an ordered fashion), and the Ca, Sr, or Eu atoms in $\frac{3}{4}$ of the available octahedral holes, as schematically shown in Figure 1. This description can be summarized in the following formula: $[\text{E}_3\Box]^\text{oct}[\text{Na}_3\Box_4\text{Tr}]^\text{tet}\text{Pn}_4$ (the $\Box$ symbol denotes a vacant site). A subtle distortion of the *hcp* packing should be noted though—the *c/a* ratio varies between 0.760 and 0.783, instead of the ideal $1.633/2 = 0.816$.

Fig. 2. Schematic representation of the hexagonal structure of $\text{Na}_3\text{E}_3\text{TrPn}_4$ ($\text{Tr} = \text{Al, Ga, In}$; $E = \text{Ca, Sr, Eu}$; $\text{Pn} = \text{P, As, Sb}$), projected approximately down the $[001]$ direction in panel a), and down the $[110]$ direction in panel b). The Na, E, Tr, and Pn atoms are drawn as red, green, yellow, and blue spheres, respectively. In panel b), the thin lines connecting the Na atoms and the Pn atoms are to emphasize the structural relationship to the wurtzite structure. The position of the Tr atoms is slightly exaggerated for the purpose to make this analogy more clearly seen.

Projections of the $\text{Na}_3\text{E}_3\text{TrPn}_4$ ($\text{Tr} = \text{Al, Ga, In}$; $\text{E} = \text{Ca, Sr, Eu}$; $\text{Pn} = \text{P, As, Sb}$) structure viewed approximately down the [001], and the [110] directions are shown in Figure 2 and Figure 3. The representation along the [001] direction highlights a single layer of isolated $[\text{TrPn}_4]^{9-}$ tetrahedral anions, separated by the Na^+ and E^{2+} cations. Figure 3a shows the details of the local coordination environments in the structure. Each $[\text{TrPn}_4]^{9-}$ anion is embedded within a matrix of nine Na^+ cations (each Pn atom connects to three Na atoms and one Tr atom in a tetrahedral fashion). The E^{2+} cations, as discussed already are found in octahedral holes of Pn atoms, but can be also seen as arranged in columns of slightly distorted trigonal prisms, sharing their trigonal faces. Two conjoined E_6 -prisms encapsulate each TrPn_4 tetrahedron—the Tr and the Pn_2 atoms are positioned inside each trigonal prism; the open rectangular faces are capped by three Na and three Pn_1 atoms, respectively.

In Figure 2b, the structural representation along the [110] direction depicts another view of the wurtzite-like lattice made up of Na, Tr , and Pn atoms, whereby some degree of covalency of the Na– Pn bonding is presumed. Table 5 shows relevant interatomic distances in representative phosphide, arsenide, and antimonide, which affirm this notion. As seen from the tabulated values, the shortest Na– Pn distances are 2.85 Å, 2.91 Å, and 3.07 Å for Na–P, Na–As, and Na–Sb, respectively. Given that the Pauling single-bonded radii [31] of the pnictogen elements are as follows: $r_{\text{P}} = 1.10$ Å, $r_{\text{As}} = 1.21$ Å, and $r_{\text{Sb}} = 1.391$ Å, and that the Pauling single-bonded and metallic radii of Na are 1.572 Å and 1.896 Å, respectively, it is apparent that simple localized/delocalized models will be inadequate to describe the nature of the Na– Pn bonding. By comparison, the Tr – Pn distances are more in-line with the covalent bonding picture. Specifically, the In–P distances are in the narrow range of 2.569(2) Å to 2.617(4) Å (Table 5), approximately 2–3% longer than the sum of the respective single-bonded Pauling radii ($r_{\text{In}} + r_{\text{P}} = 1.421 + 1.10 = 2.521$ Å) [31]; the In–As distances are 2.647(1) Å and 2.708(2) Å, i.e., 1–3% longer than the sum of the respective single-bonded Pauling radii ($r_{\text{In}} + r_{\text{As}} = 1.421 + 1.21 = 2.631$ Å); the In–Sb distances are also falling in a narrow range from 2.832(1) Å to 2.901(3) Å (Table 5), well matching the sum of their single-bonded Pauling radii ($r_{\text{In}} + r_{\text{Sb}} = 1.421 + 1.391 = 2.812$ Å). The above considerations are indicative of appreciable covalent character of the In–P, In–As, and In–Sb bonding. Same trends are observed for all re-

Table 5

Selected interatomic distances and angles in $\text{Na}_3\text{Sr}_3\text{InP}_4$, $\text{Na}_3\text{Sr}_3\text{InAs}_4$, and $\text{Na}_3\text{Sr}_3\text{InSb}_4$.

Na ₃ Sr ₃ InP ₄			Na ₃ Sr ₃ InAs ₄			Na ₃ Sr ₃ InSb ₄				
Atomic pair		Distance/Å	Atomic pair		Distance/Å	Atomic pair		Distance/Å		
In–	P1 ×3	2.569(2)	In–	As1 ×3	2.647(1)	In–	Sb1 ×3	2.832(1)		
	P2	2.617(4)		As2	2.708(2)		Sb2	2.901(3)		
P1–	In	2.569(2)	As1–	In	2.647(1)	Sb1–	In	2.832(1)		
	Na ×2	2.851(3)		Na(A) ×2	2.905(7)		Na(A) ×2	3.075(6)		
	Na	3.030(6)		Na(B) ×2	2.98(3)		Na(B) ×2	3.07(1)		
	<i>E</i> ×2	3.129(2)		Na(A)	3.07(1)		Na(A)	3.26(1)		
P2–	In	2.617(4)	<i>E</i> ×2		3.215(2)	<i>E</i> ×2		3.389(2)		
	Na ×3	3.249(7)		As2–	In		2.708(2)	Sb2–	In	2.901(3)
	<i>E</i> ×3	3.115(3)			Na(B) ×3		3.02(1)		Na(B) ×3	3.24(3)
<i>E</i> –	Na ×2	3.403(3)		Na(A) ×3	3.37(4)		Na(A) ×3	3.32(1)		
				<i>E</i> ×3	3.190(2)		<i>E</i> ×3	3.420(3)		
			<i>E</i> –	Na(B) ×2	3.38(3)	<i>E</i> –	Na(B) ×2	3.22(2)		
				Na(A) ×2	3.48(1)		Na(A) ×2	3.531(8)		
P1–In–P1		111.34(6)°	As1–In–As1		111.77(4)°	Sb1–In–Sb1		111.85(4)°		
P1–In–P2		107.53(6)°	As1–In–As2		107.06(5)°	Sb1–In–Sb2		106.98(5)°		

ported structures, and in all cases, the numerical values for the lengths of the $Tr-Pn$ bonds compare well with those reported for other ternary $A-Tr-Pn$ and $E-Tr-Pn$ phases (A = alkali metals; E = alkaline-earth metals) with related structures [11,32-34]

Fig. 3. Local coordination environments in the $Na_3E_3TrPn_4$ (Tr = Al, Ga, In; E = Ca, Sr, Eu; Pn = P, As, Sb) structure, where the atoms are represented with the respective anisotropic displacement parameters (90% probability level). Panel a) shows the structure of $Na_3Ca_3AlP_4$, which is refined as a line compound devoid of disorder; panel b) shows the structure of $Na_3Eu_3AlSb_4$, which is refined without treatment of the possible occupational and positional disorder at the Eu and Na sites; panel c) shows the final refinement of $Na_{3.41(1)}Eu_{2.59}AlSb_4$, where Na and Eu are mixed at the Eu site, and the Na site is split. The atoms are labeled, and the unit cells are outlined. The closest Na–P, Na–Sb, E–P, and E–Sb contacts are depicted. Relevant distances are listed in Table 5.

The $Pn-Tr-Pn$ angles range from ca. 108° to ca. 112° , attesting for a slight distortion from the ideal tetrahedral geometry. The angular range in the $\text{Na}_3\text{Sr}_3\text{InAs}_4$ and $\text{Na}_3\text{Sr}_3\text{InSb}_4$ structures is almost a full degree wider than in $\text{Na}_3\text{Sr}_3\text{InP}_4$ (Table 5), which could suggest that the somewhat greater distortion of the InAs_4 - and InSb_4 -tetrahedra is a response to a structural disorder involving not the unit themselves, but rather, the “solvating” cations. Another hint for possible occupational /positional disorder on the cation sites is the behavior of the respective anisotropic displacement parameters of the Na and Sr atoms.

The structural representations in Figure 3 use thermal ellipsoids drawn at the 90% probability level, and the side-by-side views are a telltale sign of disorder. In the structure of $\text{Na}_3\text{Ca}_3\text{AlP}_4$, the one with the smallest unit cell volume of all (Table 1), which is refined as a line compound devoid of any disorder (Figure 3a), there are appear to be no anomalies in the anisotropic displacement parameters. Isoelectronic substitution of Ca^{2+} with Eu^{2+} leads to an enlargement of the unit cell by almost $40 \text{ \AA}^3$, coupled with refinement data showing problematic displacement parameters at the Eu site—as a result $\text{Na}_{3.12(1)}\text{Eu}_{2.88}\text{AlP}_4$ is the first refinement that unambiguously confirms random mixing of Na and Eu [35]. Small Na and Ca disorder could also be present for $\text{Na}_3\text{Ca}_3\text{InP}_4$, but co-occupation of Na and Ca at the same site could not be reliably established.

The remaining two phosphides and three of the arsenides show the exact same occupational disorder—nearly one of every ten Ca, Sr, or Eu atoms are statistically replaced by Na atoms. It is not until the refinement of $\text{Na}_{3.34(2)}\text{Sr}_{2.66}\text{InAs}_4$ (unit cell volume over $625 \text{ \AA}^3$, 22.3% larger than $\text{Na}_3\text{Ca}_3\text{AlP}_4$), when the signature of another disorder becomes apparent—positional disorder at the Na site. This disorder persists in all antimonides, and the way the disorder is modeled and the resulting changes in the refinement parameters are summarized in Table 6.

Table 6

Selected structure refinement parameters for $\text{Na}_3\text{Eu}_3\text{AlSb}_4$, refined without Na and Eu mixing at the Eu site, and without taking into a consideration the possible positional disorder at the Na site, compared with the data for $\text{Na}_{3.41(1)}\text{Eu}_{2.59}\text{AlSb}_4$, where the disorder at both the Eu and the Na site is modeled.

Na ₃ Eu ₃ AlSb ₄			Na _{3.41(1)} Eu _{2.59} AlSb ₄		
Final R1 (<i>I</i> >2σ _{<i>I</i>})		R1 = 0.0305 wR2 = 0.1046	Final R1 ^a (<i>I</i> >2σ _{<i>I</i>})		R1 = 0.0157 wR2 = 0.0396
Goodness of fit		1.208	Goodness of fit		1.116
Largest diff. peak & hole /e [−] Å ^{−3}		2.68 & −2.29	Largest diff. peak & hole /e [−] Å ^{−3}		0.69 & −0.91
Principal mean-square atomic displacements, <U _{<i>ij</i>} ² >					
Na	0.0825, 0.0420, 0.0203		Na(A)/Na(B)	0.0413	
Eu	0.0324, 0.0238, 0.0189		Eu/Na	0.0290, 0.0211, 0.0153	
Al	0.0115, 0.0115, 0.0074		Al	0.0180, 0.0136, 0.0136	
Sb1	0.0207, 0.0131, 0.0120		Sb1	0.0234, 0.0158, 0.0147	
Sb2	0.0158, 0.0158, 0.0120		Sb2	0.0187, 0.0187, 0.0146	
Atomic pair		Distance/Å	Atomic pair		Distance/Å
Al–	Sb1 ×3	2.691(2)	Al–	Sb1 ×3	2.692(1)
	Sb2	2.771(7)		Sb2	2.761(3)
Sb1–	Na ×2	3.055(4) (×2)	Sb1–	Na(B) ×2	3.03(1)
	Eu ×2	3.400(1) (×2)		Na(A) ×2	3.073(2)
Sb2–	Na ×3	3.26(1) (×3)	Sb2–	Na(A)	3.241(5)
	Eu ×3	3.402(1) (×3)		<i>E</i> ×3	3.3373(5)
		Na(B) ×3		3.20(3)	
		Na(A) ×3		3.316(6)	
		<i>E</i> ×3		3.4067(6)	

This is done on the example of $\text{Na}_3\text{Eu}_3\text{AlSb}_4$, where the improvements appear to be considerable. Initially, a refinement of $\text{Na}_3\text{Eu}_3\text{AlSb}_4$ as a line compound was carried out, yielding very elongated anisotropic displacement parameters for Na (as illustrated in Figure 3b, $U_{33} \gg U_{11}$). Subsequent refinement where Na and Eu are mixed at the Eu site, and the Na site is split leads to the chemical formula $\text{Na}_{3.41(1)}\text{Eu}_{2.59}\text{AlSb}_4$, as well as much improved residuals and more uniform displacement parameters (Table 6 and Figure 3c).

We speculate that the Na site split can be modeled in our refinements only in the structures with the largest unit cell volumes (i.e., all antimonides) because there is “room” for the Na atom to be present in both off-centered positions. The majority and minority sites are almost always in a 2:1 to 3:1 ratio, and both sites have relatively close contacts with neighboring *Pn* atoms, which are fully occupied (Table 5). Notice as well the effect the splitting has on the anisotropic displacement parameters for the *Pn1* and *Pn2* atoms (Figure 3c). Apparently, in the structures with the smallest volumes, the coordination polyhedra are very tight, meaning that if such disorder were to exit, it will be on a very small scale, and very difficult to be accounted for.

Lastly, we would like to comment on the implications the cation disorder has on the chemical bonding and the valence electron count. A fully ordered $\text{Na}_3E_3\text{TrPn}_4$ (*Tr* = Al, Ga, In; *E* = Ca, Sr, Eu; *Pn* = P, As, Sb) structure is a valence compound that can be rationalized as $[\text{Na}^+]_3[\text{E}^{2+}]_3[\text{TrPn}_4]^{9-}$, following the octet rule. As such, all stoichiometric 3-3-1-4 materials will have closed-shell configurations for all atoms and should exhibit intrinsic semiconducting behavior, i.e., they will be classic Zintl phases. Partial replacement of the divalent *E* atoms by Na will lead to a perceived shortage of valence electrons—for example, in the most extreme case of $\text{Na}_{3.59(1)}\text{Eu}_{2.41}\text{GaSb}_4$, the partitioning must follow the $[\text{Na}^+]_{3.6}[\text{Eu}^{2+}]_{2.4}[\text{GaSb}_4]^{9-}[\text{h}^+]_{0.6}$ formula, which suggests that more than 1/2 electron is needed to achieve electron balance. $\text{Na}_{3.59(1)}\text{Eu}_{2.41}\text{GaSb}_4$ is not the only structure where *E* atoms are partially replaced by Na—in fact, 12 of the herein reported 15 compounds show the same phenomenology and their refined compositions reflect the off-stoichiometric formula $\text{Na}_{3+x}E_{3-x}\text{TrPn}_4$ ($0 < x < 0.6$). Most of the previously reported $\text{Na}_4E_2\text{TiPn}_4$ and $\text{K}_4E_2\text{TiPn}_4$ (*E* = Ca, Sr, Ba, Eu; *Ti* = Si, Ge, Sn; *Pn* = P, As, Sb) [36] are also off-stoichiometric, with similar levels Na-Sr and Na-Eu mixing, i.e., $\text{Na}_{4+x}E_{2-x}\text{TiPn}_4$ ($0 < x < 0.4$). Notably, the $\text{Na}_3\text{Ca}_3\text{TrP}_4$ (*Tr* = Al, Ga, In) and $\text{K}_4\text{Ba}_2\text{TiPn}_4$ (*Ti* = Ge, Sn; *Pn* = P, As, Sb, Bi) do not show such disorder. We also need to mention that whether one considers the scenario with random distribution of different cations on the same crystallographic site, or defects on the divalent site [35], both cases, $\text{Na}_{3+x}E_{3-x}\text{TrPn}_4$ and $\text{Na}_3[\text{E}_{3-x}\square_x]\text{TrPn}_4$, represent electron-deficient formulae.

The origins of this effect are not yet understood. Clearly, there is an interplay between packing and electronic requirements, as can be discerned from the apparent correlations between the corresponding interatomic distances, atomic sizes and electronegativities, and the structural disorder. Unrecognized Nb-contamination could account for the lower than expected valence electron count, as Nb(V) substituting for Al, Ga or In will bring in extra electrons, as shown on the example of $\text{Na}_{3.12}\text{Sr}_{2.88}\text{Al}_{0.94}\text{Nb}_{0.06}\text{P}_4$ [28]. However, the levels of Na-Eu Na-Sr admixture we report are much higher than that, and clearly, 10-20% Nb-substitution will not be plausible in the context of our refinements. Another possibility concerns mixed valency, which is certainly applicable to the Eu-containing compounds. Eu could exist as Eu(II) or Eu(III), thereby compensating the electron-deficiency that results from the disorder. This anomalous behavior has been demonstrated already on the examples of $\text{Na}_4\text{Eu}_2\text{TiAs}_4$ and $\text{Na}_{4.3}\text{Eu}_{1.7}\text{TiAs}_4$, which show different magnetic behavior [37], with the latter achieving Zintl phase like electron balance by having 1/6 of the Eu atoms in the higher oxidation state. Such mixed-valent configurations are possible for our $\text{Na}_{3+x}\text{Eu}_{3-x}\text{TrPn}_4$ samples too, but this supposition could not be experimentally verified since phase-pure material for magnetic susceptibility measurements could not be obtained.

Valence fluctuations cannot exist for Ca and Sr, leaving the hypothesis for substantial covalent contribution of the “cations” to the overall bonding. This was mentioned already along the lines of the short Na–*Pn* distances and the structural relationship between this arrangement and the wurtzite-type structure. The results from the electronic band structure calculations and the analysis of the bonding from this more sophisticated point of view, discussed in the following paragraphs, shed more light on this conundrum.

3.3. Electronic structure

TB-LMTO-ASA electronic band structure calculations were carried out for idealized and devoid of disorder $\text{Na}_3\text{Sr}_3\text{InP}_4$, $\text{Na}_3\text{Sr}_3\text{InAs}_4$ and $\text{Na}_3\text{Sr}_3\text{InSb}_4$. For the cases where splitting on the Na sites was apparent (viz. $\text{Na}_3\text{Sr}_3\text{InAs}_4$ and $\text{Na}_3\text{Sr}_3\text{InSb}_4$) the electronic structure of two other idealized “ordered” models were calculated, each assuming that either Na(A) or Na(B) sites are fully occupied. This was done in order to examine the electronic structure in detail, and to compare and contrast the chemical bonding among phosphides (anticipated most ionic bonding), arsenides, and antimonides (anticipated most covalent bonding) with the same cations.

Fig. 4. Calculated total density of states (DOS) and partial density of states (PDOS) curves for $\text{Na}_3\text{Sr}_3\text{InP}_4$, $\text{Na}_3\text{Sr}_3\text{InAs}_4$ and $\text{Na}_3\text{Sr}_3\text{InSb}_4$. The Fermi level is the energy reference at 0 eV.

Separate sets of calculations were carried out for idealized and devoid of disorder $\text{Na}_3\text{Ca}_3\text{AlP}_4$, $\text{Na}_3\text{Ca}_3\text{GaP}_4$ and $\text{Na}_3\text{Ca}_3\text{InP}_4$, aimed at better understanding of the role of the *Tr*-element within a series of phosphides.

The calculated total and partial density of states (DOS) for $\text{Na}_3\text{Sr}_3\text{InP}_4$, $\text{Na}_3\text{Sr}_3\text{InAs}_4$ and $\text{Na}_3\text{Sr}_3\text{InSb}_4$ are displayed in Figure 4. Confirming the Zintl phase rationalization, as described above, band-gaps are observed in all cases. The speculated trend concerning the change in the electronic properties on going from $\text{Na}_3\text{Sr}_3\text{InP}_4$ to $\text{Na}_3\text{Sr}_3\text{InSb}_4$ is noticeable immediately—the states around the Fermi level are very much alike, with the gap closing in the order P-As-Sb. These results correlate well with the electronic properties of the previously reported Ba_2ZnPn_2 [38] family. Similar results were obtained for the series $\text{Na}_3\text{Ca}_3\text{AlP}_4$, $\text{Na}_3\text{Ca}_3\text{GaP}_4$ and $\text{Na}_3\text{Ca}_3\text{InP}_4$, where the gap was found closing in the order Al-Ga-In. These findings, simply put, are in line with basic periodic properties—the decrease in electronegativities in P, As, and Sb, on one hand, and the increase in electronegativities of Al, Ga, and In, on the other [31].

Just below Fermi level, the band contributions are mainly from *p* and *d* orbitals from Na and Sr, as well as *p* bands from In and *Pn* atoms (Figure 4 and Figures 2, 3, and 4 in supporting information). The distributions of all bands are similar to each other. The crystal orbital Hamilton populations (COHP) of selected interactions also show that the bonding is optimized, transitioning from bonding to antibonding character above the Fermi level (Figure 5). The COHP curves indicate too that in all structures, the narrow bands *ca.* 3 eV below the Fermi level are most closely related with the interactions within the $[\text{InPn}_4]$ anions and are composed of mainly *Pn p*-orbitals. The states closer to the Fermi level, which should play the most important role in determining the electronic transport properties, are dominated by *Pn p*-orbitals and Sr *4d*-orbitals, with small contributions from Na as well. Mixing of Sr and *Pn* orbitals in the valence band is indicative of the appreciable covalency of the Sr–*Pn* interactions. Na–*Pn* COHP is arguably the weakest, but not negligible, in line with the idea that there is some degree of covalency even in the Na–*Pn* bonding. Therefore, fully charge transfer from the cations to the anions should not be expected, a notion that is somewhat negating the applicability of the classic Zintl-Klemm concept towards these structures.

Fig. 5. COHP curves for selected interactions in the idealized structures of $\text{Na}_3\text{Sr}_3\text{InP}_4$, $\text{Na}_3\text{Sr}_3\text{InAs}_4$ and $\text{Na}_3\text{Sr}_3\text{InSb}_4$. In the –COHP diagrams, the areas with white and yellow background represent the bonding and antibonding states, respectively. The Fermi level is the energy reference at 0 eV.

Based on the above, all $\text{Na}_3\text{Ca}_3\text{TrPn}_4$, $\text{Na}_3\text{Sr}_3\text{TrPn}_4$, and $\text{Na}_3\text{Eu}_3\text{TrPn}_4$ ($\text{Tr} = \text{Al, Ga, In; Pn} = \text{P, As, Sb}$), would be expected to exhibit intrinsic semiconducting behavior. However, given that the arsenides and the antimonides, in particular, deviate from the ideal stoichiometry, poor metallic behavior is more likely in those cases. The total and the partial DOS curves in Fig. 4 and the COHP curves in Fig. 5 do not provide clues to help understand why the structure refinements for several members indicate mixing of cations, which apparently leads to less than optimal valence electron count.

In this regard, the disorder issues (Na/Sr mixing at the Sr site and splitting of the Na position (Na(A) and Na(B))) are not addressed by these model calculations (or this level of theory). According to the experimental

results, Sr would be partially substituted by Na to a far greater extent (i.e., more obvious from the single-crystal refinements) for the Sb analogues than for the P analogues. Besides a change in the electronegativity, i.e., implied change in the *Pn* bonding polarization, a change in the atomic sizes is also apparent. We recall that Na/Sr mixing lowers the valence electron count, which is at the optimal range based on the electronic structure analysis, as discussed above. However, since the atomic radius of Na is smaller than that of Sr, such substitution affects not only the electronic structure, but also the crystal packing. This implies that in addition to electronic, other factors may contribute to the Na and Sr disorder in this system.

For the Na splitting, as in the cases of $\text{Na}_3\text{Sr}_3\text{InAs}_4$ and $\text{Na}_3\text{Sr}_3\text{InSb}_4$, the main features of the electronic structures of $\text{Na}(\text{B})_3\text{Sr}_3\text{InAs}_4$ and $\text{Na}(\text{B})_3\text{Sr}_3\text{InSb}_4$ (Figure S1 in supporting information) are very similar to that of $\text{Na}(\text{A})_3\text{Sr}_3\text{InAs}_4$ and $\text{Na}(\text{A})_3\text{Sr}_3\text{InSb}_4$. Thus, the main reason for Na splitting may be attributed to the larger unit cell of $\text{Na}_3\text{Sr}_3\text{InAs}_4$ and $\text{Na}_3\text{Sr}_3\text{InSb}_4$, compared to $\text{Na}_3\text{Sr}_3\text{InP}_4$ or any of the Ca-analogues. We also note that the integrated COHP values for $\text{Na}(\text{A})\text{--As}$ (0.032) and $\text{Na}(\text{A})\text{--Sb}$ (0.035) are slightly larger than those of $\text{Na}(\text{B})\text{--As}$ (0.027) and $\text{Na}(\text{B})\text{--Sb}$ (0.031), respectively (the larger *i*COHP values are indicating stronger bonding interaction, which can also be inferred from the corresponding interatomic distances). This could be the reason for the higher refined occupancy of Na(A) and Na(B) in both $\text{Na}_3\text{Sr}_3\text{InAs}_4$ and $\text{Na}_3\text{Sr}_3\text{InSb}_4$. Additional experimental and theoretical work is needed to fully understand the origins of this unconventional behavior in these ostensibly simple structures.

Conclusion

With the present study, the crystal and electronic structures of 15 quaternary compounds with common formula $\text{Na}_3\text{E}_3\text{TrPn}_4$ ($\text{E} = \text{Ca}, \text{Eu}, \text{Sr}$; $\text{Tr} = \text{Al}, \text{Ga}, \text{In}$; $\text{Pn} = \text{P}, \text{As}, \text{Sb}$) are detailed. All structures are refined from single-crystal X-ray diffraction data and demonstrated Na/E disorder except for $\text{Na}_3\text{Ca}_3\text{AlP}_4$, $\text{Na}_3\text{Ca}_3\text{GaP}_4$ and $\text{Na}_3\text{Ca}_3\text{InP}_4$. Additionally, the refined models for the majority of arsenides and especially the antimonides further suggest that Na is also disordered and this can be modeled as a split between two positions (i.e., Na(A) and Na(B)) in the structure. The electron count in the idealized formula $\text{Na}_3\text{E}_3\text{TrPn}_4$ for this family suggests close-shell configurations for all atoms, which is a trait of the classic Zintl phases. This is also supported by the electronic band structure calculations, which show that these are valence compounds with distinct band gaps between valence band and conduction band. The discovery of these Na–E–Tr–Pn quaternary members has proven that the number of new phases in this system is far from been exhausted and further exploratory work to unravel their potentially rich crystal chemistry is called for.

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- [35] We need to mention that another hypothesis was also considered as a possible explanation for the problems with the Eu displacement parameter in this structure, namely, the existence of vacancies. Unfortunately, the difference in the numerical values for the scenario $\text{Na}_3[\text{Eu}_{2.88}\text{Na}_{0.12(1)}]\text{AlP}_4$ vs $\text{Na}_3[\text{Eu}_{2.91}\square_{0.09(1)}]\text{AlP}_4$ (the $\square$ symbol denotes a vacancy) is not statistically significant. The same problem was encountered for the refinements of the Na-Eu-Al-Sb sample, where modeling the experimental data with and without a disorder shows the most dramatic improvement (Table 6 in the text). In this case, $\text{Na}_3[\text{Eu}_{2.59}\text{Na}_{0.41(1)}]\text{AlSb}_4$ vs $\text{Na}_3[\text{Eu}_{2.74}\square_{0.26(1)}]\text{AlSb}_4$ also did not show a statistical preference for one model over the other. Similar results were obtained for all other refined structures. Given how close the compositions from the two different scenario are, elemental microanalysis by energy-dispersive X-ray spectroscopy could not help differentiate between the two limiting cases. We adopted the model with disorder and rejected the model with vacancies for all refined structures based on the well-established crystal chemistry for the already known members. To this end, there are no known precedents for vacancies in this structural family, yet, random distribution of different cations on the same crystallographic site is common.
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Appendix A.

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc..... The information consists of CIFs for all reported structures, as well as plots of DOS and COHP for $\text{Na}_3\text{Sr}_3\text{InAs}_4$ and $\text{Na}_3\text{Sr}_3\text{InSb}_4$, two cases where splitting on the Na sites was apparent and the electronic structures were calculated for “ordered” models, each assuming that either Na(A) or Na(B) sites were fully occupied. Plots of partial DOS for $\text{Na}_3\text{Sr}_3\text{InP}_4$, $\text{Na}_3\text{Sr}_3\text{InAs}_4$ and $\text{Na}_3\text{Sr}_3\text{InSb}_4$, showing the contributions of all orbitals are also supplied.