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Valence Compounds versus Metals. Synthesis, Characterization, and Electronic Structures of Cubic $\text{Ae}_4\text{Pn}_3$ Phases in the Systems $\text{Ae} = \text{Ca, Sr, Ba, Eu}; \text{Pn} = \text{As, Sb, Bi}$

Ban Li
Iowa State University

Anja V. Mudring
Iowa State University, mudring@iastate.edu

John D. Corbett
Iowa State University

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Valence Compounds versus Metals. Synthesis, Characterization, and Electronic Structures of Cubic Ae4Pn3 Phases in the Systems Ae = Ca, Sr, Ba, Eu; Pn = As, Sb, Bi

Abstract
The isostructural compounds Sr₄Bi₃, Ba₄Bi₃, and Ba₄As₂.₆₀ were prepared by direct reactions of the corresponding elements and their structures determined from single-crystal X-ray diffraction data as anti-Th₃P₄ type in the cubic space group I₄̅3d, Z = 4 (a = 10.101(1) Å, 10.550(1) Å, 9.973 (1) Å, respectively). The two bismuth compounds are stoichiometric, and the arsenide refines as Ba₄As₂.₆₀(2). Only unrelated phases are obtained for all binary combinations among the title components for either Ca or Sb. The magnetic susceptibility and resistivities of Ba₄Bi₃ and Eu₄Bi₃ show that they are good metallic conductors (∼40 μΩ·cm at 298 K), whereas Ba₄As₂.₆₀ exhibits ρ₁₅₀ > 1000 μΩ·cm. The electronic structures of Sr₄Bi₃, Ba₄Bi₃, and Ba₄As₃ were calculated by TB-LMTO-ASA methods. Mixing of cation d states into somewhat disperse valence p bands on Bi results in empty bands at E_F and metallic behavior, whereas the narrower valence band in the electron-deficient Ba₄As₃ leads to vacancies in about 11% of the anion sites and a valence compound.

Keywords
Department of Chemistry

Disciplines
Metallurgy | Other Materials Science and Engineering | Process Control and Systems

Comments
Introduction

R₄Pₙₙ phases for R = rare-earth element, Pₙ (pnictogen) = As, Sb, Bi, are known to crystallize in the anti-Th₃P₄ type structure, especially for the larger metals La–Tb and Yb. These compounds and their solid solutions have been extensively investigated because of their interesting magnetic and electronic properties. For example, the Gd compounds are ferromagnets, the Ce compounds show interesting Kondo-type behaviors, and the Yb compounds show valence fluctuation. The bonding or, more precisely, the valence of these phases can be successfully rationalized in terms of electron count for this stoichiometry and structure in most of these phases can be successfully rationalized in terms of simple octet bonding schemes. Thus, for these pnictide compounds to be valence precise at least one of the four (crystallographically equivalent) rare-earth metal atoms must have an oxidation state of +3. (A higher fraction presumably yields a metallic phase.) For example, Sm₄Bi₃, Yb₄As₃, and Yb₄Bi₃ are mixed-valent materials with a 1:3 ratio of trivalent and divalent rare-earth ions. An interesting pressure-induced valence instability was established for Sm₄Bi₃, wherein the Sm⁺³ atoms shift toward the Sm⁺² state, and the material goes from semimetallic to a metallic state in the transition.

Up to now, only a few pnictides with anti-Th₃P₄ type structures have been reported with nominally divalent cations: Eu₄Bi₃, Ba₄P₉ (≡Ba₄P₃₆₇), and Ba₄As₄Au. In Ba₄As₄Au, five As⁻³ and one Au⁺ disordered over the single anion site. For Eu₄Bi₃, the presence of the stoichiometric composition with only divalent cations was established by the effective magnetic moment, which suggested that the compound was deficient by one electron per formula unit.

The isostructural compounds Sr₄Bi₃, Ba₄Bi₃, and Ba₄As₂.60 were prepared by direct reactions of the corresponding elements and their structures determined from single-crystal X-ray diffraction data as anti-Th₃P₄ type in the cubic space group I43d, Z = 4 (a = 10.101(1) Å, 10.550(1) Å, 9.973 (1) Å, respectively). The two bismuth compounds are stoichiometric, and the arsenide refines as Ba₄As₂.60. Only unrelated phases are obtained for all binary combinations among the title components for either Ca or Sb. The magnetic susceptibility and resistivities of Ba₄Bi₃ and Eu₄Bi₃ show that they are good metallic conductors (~40 μΩ·cm at 298 K), whereas Ba₄As₂.60 exhibits ρ₅⁰ > 1000 μΩ·cm. The electronic structures of Sr₄Bi₃, Ba₄Bi₃, and Ba₄As₃ were calculated by TB-LMTO-ASA methods. Mixing of cation d states into somewhat disperse valence p bands on Bi results in empty bands at EF and metallic behavior, whereas the narrower valence band in the electron-deficient Ba₄As₃ leads to vacancies in about 11% of the anion sites and a valence compound.

Valence Compounds versus Metals. Synthesis, Characterization, and Electronic Structures of Cubic Ae₄Pₙₙ Phases in the Systems Ae = Ca, Sr, Ba, Eu; Pₙ = As, Sb, Bi

Bin Li, Anja-Verena Mudring, and John D. Corbett*  

Ames Laboray-DOE and Department of Chemistry, Iowa State University, Ames, Iowa 50011

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* To whom correspondence should be addressed. E-mail: jdc@ameslab.gov.

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This was considered to be consistent with the measured metallic behavior, although the room temperature resistivity, about 1.29(1) Ω-cm, seems much too high for this type of compound. (Anomalous magnetic and electronic behavior had been reported before for this compound.) For Ba₃P₂, the positional parameter of phosphorus in a defect anti-Th₃P₃ type structure was refined only from powder pattern data, with an assumed occupancy for P of \( \frac{2.071}{2} = 0.89 \) in analogy with the known inverse (C-type) Ce₂S₃ in this structure type. A black color but a high resistivity were also reported. Thus, phases with divalent cations in pnictides with this type structure should, if stoichiometric, be one electron deficient and metallic, whereas if they are substoichiometric as Ae₄Pₙ₃, they might reasonably be assumed to be closed shell and semiconductors.

There have been no published results regarding such compounds between Ca, Sr, or Ba and Sb or Bi. However, we were encouraged to make the present study by the unpublished accidental discoveries of nominal Ba₄As₃, Sr₄Bi₃, and Ba₄Bi₃ in this structure type during an exploration for compounds analogous to Ca₁₆Sb₁₁. A diffraction study of the last example in the subgroup R₃c also suggested that it was fully stoichiometric. The present compounds are not to be confused with the orthorhombic (Pbam) Sr₂As₅ and Ba₃P₂ phases. In order to understand the stoichiometries and electronic properties of these anti-Th₃P₃ type pnictides, we have examined the syntheses and physical properties of A₄Pₙ₃ compounds for A = Ca, Sr, Ba, Eu with, in part, Pn = As, Sb, and Bi. We also report a density-functional-theory study of the electronic structure of several members of this series.

**Experimental Section**

**Syntheses.** All operations were carried out in a N₂-filled glovebox with the moisture level below 1 ppm. The compositions Ba₄Bi₃, Sr₄Bi₃, Ba₄As₃.67, and Eu₄Bi₃ were synthesized from stoichiometric mixtures of the following elements: Ba (99.9%), Sr (99.9%), As (99.99%), Bi (99.999%), (all from Alfa-Aesar), and Eu (99.9% total, Ames Laboratory). Mixtures were loaded in niobium containers that were sealed by arc welding under argon and then enclosed in fused silica ampules that were in turn evacuated and flame-sealed. All compounds except Eu₄Bi₃ could be prepared by the following process: About 300 mg of the appropriate mixture was first heated to 700 °C and held for 6 h; then, the temperature was increased to 1050 °C, held for 6 h, and quenched to room temperature. The sample was reheated at 800 °C for 140 h and finally cooled to room temperature at 3 °C/h. Pure Eu₄Bi₃ can be easily obtained by simply quenching after reaction at 1100 °C for 36 h. All compounds are dark and brittle and very air sensitive. X-ray powder patterns (Enraf-Nonius 552 Guinier camera, Cu Kα radiation, \( \lambda = 1.540562 \) Å, and NIST silicon as an internal standard) were used for phase analyses of the products. Pure phases (to X-rays) were obtained for the Ba₄Bi₃, Eu₄Bi₃, and Ba₄As₂.67 compositions, whereas a Ba₄-

**Table 1. Crystallographic Data for Ae₄Pₙ₃**

<table>
<thead>
<tr>
<th></th>
<th>Ba₄Bi₃</th>
<th>Sr₄Bi₃</th>
<th>Ba₄As₂.67</th>
</tr>
</thead>
<tbody>
<tr>
<td>( f_w )</td>
<td>1176.3</td>
<td>977.42</td>
<td>743.4</td>
</tr>
<tr>
<td>space group, Z</td>
<td>( \text{I43d (No.220)} ), 4</td>
<td>( \text{I43d (No.220)} ), 4</td>
<td>( \text{I43d (No.220)} ), 4</td>
</tr>
<tr>
<td>( a (\text{Å}) )</td>
<td>10.550(1)</td>
<td>10.101(1)</td>
<td>9.973(1)</td>
</tr>
<tr>
<td>( V (\text{Å}^3) )</td>
<td>1174.73(2)</td>
<td>1030.66(2)</td>
<td>992.02(2)</td>
</tr>
<tr>
<td>( \rho (\text{Mg/m}^3) )</td>
<td>6.653</td>
<td>6.299</td>
<td>4.978</td>
</tr>
<tr>
<td>( \mu (\text{mm}^{-1}) )</td>
<td>57.906</td>
<td>71.492</td>
<td>24.15</td>
</tr>
<tr>
<td>( R_1/\text{w}R_2 (I &gt; 2\sigma(I)) )</td>
<td>0.034/0.078</td>
<td>0.038/0.065</td>
<td>0.021/0.047</td>
</tr>
</tbody>
</table>

As₄ stoichiometry also produced about 15% of an unknown. The highest yield of Sr₄Bi₃ was about 85% plus the very stable Sr₄Bi₁₀. Attempts to produce the isostructural antimonides for Ca, Sr, and Ba as well as Ca₄Bi₃, failed, giving the corresponding known Ae₄Pₙ₃ phases with the Ho₁₁Ge₁₀ type structure in ~95% yields. The other minor products, e.g., ~5% Ca, were not seen.

**Physical Properties.** The resistivities of Ba₄Bi₃ and Eu₄Bi₃ were examined by the electrodeless “Q” method with the aid of a Hewlett-Packard 4342A Q meter. This method is particularly suitable for measurements on highly air-sensitive samples. For this purpose, 86.1 and 104.2 mg samples of powdered Ba₄Bi₃ and Eu₄Bi₃ with grain diameters between 150 and 250 μm, respectively, were dispersed with chromatographic alumina and sealed in Pyrex tubes under He. Measurements were made at 34 MHz over the range 120—291 K. The magnetization of Ba₄Bi₃ and Eu₄Bi₃ was measured on a Quantum Design MPMS SQUID magnetometer at a field of 3 T over the temperature range 6—300 K. Typically, 30—60 mg of the sample was sealed within a fused silica tubing in which it was held between two tightly fitting rods of the same material. Corrections were applied for the holder and the ion core diamagnetism.

**Structure Determination.** Single crystals of nominal Ba₄Bi₃ (0.2 \( \times 0.25 \times 0.4 \) mm³), Sr₄Bi₃ (0.15 \( \times 0.15 \times 0.25 \) mm³), and Ba₄As₂.67 (0.11 \( \times 0.18 \times 0.07 \) mm³) were mounted in glass capillaries inside the glovebox. The crystals were first checked by Laue photography for their singularities and then transferred to a Rigaku AFC6R automatic diffractometer for data collection, which took place at room temperature with the aid of monochromated Mo Kα radiation. Cell constants and an orientation matrix for data collection were determined from least-squares refinements of the setting angles of 25 centered reflections. The diffraction data were corrected for Lorentz and polarization effects and for absorption with the aid of three \( \psi \)-scans of reflections at different 2θ values. To be sure of the refined substoichiometry Ba₄As₂.86, a second crystal (0.15 \( \times 0.18 \times 0.27 \) mm³) was selected from another synthesis, and data were collected on a SMART APEX CCD diffractometer at room temperature. All the structures were solved and refined in cubic centric I4̅3d with the aid of the SHELXTL V5.1 software package. The barium bismuthide was solved as a merohedral twin. Some details of the crystallographic and refinement parameters are given in Table 1. Table 2 contains the atomic positional and the isotropic equivalent displacement parameters, and Table 3 gives the important bond distances therein. The results reported for Ba₄S₂.602 came from the CCD data.

**Computational Details.** TB-LMTO-ASA electronic band structure calculations were carried out for Sr₄Bi₃ and Ba₄Bi₃ as well as for hypothetical Ba₄As₄ with the aid of the Stuttgart LMTO-47

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**Table 2.** Atomic Coordinates and Equivalent Isotropic Displacement Parameters for Ae₄P₃

<table>
<thead>
<tr>
<th>compd</th>
<th>atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Ueq</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba₄Bi₃</td>
<td>Ba</td>
<td>0.0730(1)</td>
<td>x</td>
<td>x</td>
<td>10(1)</td>
</tr>
<tr>
<td></td>
<td>Bi</td>
<td>3/8</td>
<td>0</td>
<td>1/4</td>
<td>9(1)</td>
</tr>
<tr>
<td>Sr₄Bi₃</td>
<td>Sr</td>
<td>0.0728(1)</td>
<td>x</td>
<td>x</td>
<td>14(1)</td>
</tr>
<tr>
<td></td>
<td>Bi</td>
<td>3/8</td>
<td>0</td>
<td>1/4</td>
<td>13(1)</td>
</tr>
<tr>
<td>Ba₄As₂.60(2)</td>
<td>Ba</td>
<td>0.0780(1)</td>
<td>x</td>
<td>x</td>
<td>30(1)</td>
</tr>
<tr>
<td></td>
<td>As^a</td>
<td>3/8</td>
<td>0</td>
<td>1/4</td>
<td>24(1)</td>
</tr>
</tbody>
</table>

*Occupancy = 0.866(7).*

**Table 3.** Selected Interatomic Distances (Å) in Ae₄P₃ Phases

<table>
<thead>
<tr>
<th></th>
<th>Ba₄Bi₃</th>
<th>Sr₄Bi₃</th>
<th>Ba₄As₂.60(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pn–Ae × 4</td>
<td>3.537(1)</td>
<td>3.384(1)</td>
<td>3.2923(6)</td>
</tr>
<tr>
<td>Pn–Ae × 4</td>
<td>3.772(1)</td>
<td>3.614(1)</td>
<td>3.6236(6)</td>
</tr>
<tr>
<td>Ae–Pn × 3</td>
<td>3.537(1)</td>
<td>3.384(1)</td>
<td>3.2923(6)</td>
</tr>
<tr>
<td>Ae–Pn × 3</td>
<td>3.772(1)</td>
<td>3.614(1)</td>
<td>3.6236(6)</td>
</tr>
<tr>
<td>Ae–Ae × 3</td>
<td>4.040(1)</td>
<td>3.870(1)</td>
<td>3.8756(7)</td>
</tr>
<tr>
<td>Ae–Ae × 2</td>
<td>4.5684(5)</td>
<td>4.3739(5)</td>
<td>4.3185(5)</td>
</tr>
</tbody>
</table>

**Results and Discussion**

**Stoichiometry.** The problem we have faced lies with the supposed (Ae₄)₃P₃ phases with the inverse Th₄P₃-type structure that may form for Ae = Ca—Ba (and Eu) and Pn = As—Bi. It is important to establish the correct stoichiometries, the related properties, and the theoretical reasons for these findings. The structure type contains only well separated Pn atoms and does not offer any suggestion of Pn–Pn bonding. Thus, if these compounds are Zintl (valence) phases, then electron conservation would require a stoichiometry and oxidation states of (Ae^2+)(Pn^-3)_{6,7}, and semiconducting (or insulating) and diamagnetic properties should follow. (This circumstance is common in the normal-valent sequisulfides and selenides of the rare-earth elements, e.g., ref 23.) On the other hand, an Ae₄P₃ stoichiometry would appear to require the presence of a hole in the pnictide valence band or equivalent, and this would presumably lead to metallic properties. Possible participation of the cations in this event would appear important. A third possibility is that one or more in this family of compounds with a 4:3 proportion and this structure type do not exist. We find that all three situations in fact occur with binary combinations of As, Sb, or Bi with the alkaline-earth metals. The actual situation with the reported black Ba₄P₂9 (Ba₄P₂_{6,7} vs Ba₄P₃) does not seem to have been clarified, although the former valence type compound seems probable.

Two approaches and ways have been utilized to differentiate A₄P₂_{6,7} from A₄P₃ formulations, semiquantitative syntheses and structural refinements. Reactions of samples loaded as Ba₄Bi₃, Eu₄Bi₃, and Sr₄Bi₃ gave the pure targets for the first two according to their Guinier powder patterns (i.e., >95% yields) and the third, 85% Sr₄Bi₃, 15% Sr₃Bi₁₀. Conversely, reactions loaded with the compositions Ba₄Bi₃ (≡Ba₄Bi₂_{6,7}) and Eu₄Bi₃ gave ~90% of the cubic M₄Bi₃ structure plus the known M₄SrBi₁ for both. Likewise, the products from loaded Ba₄As₂_{6,7} and Ba₄As₃ samples produced powder patterns for pure Ba₄As₂_{5,6} and the same plus ~15% of an unknown (presumably arsenic-richer) phase, respectively. Note that these semiquantitative synthesis features are powerful evidence for the assigned stoichiometries. In parallel, structural refinements of Ba₄Bi₃ and Sr₄Bi₃ showed that once all atoms were input, successive variations of occupation factors led to no significant changes from unity. Similarly, separate sets of diffraction data collected for different crystals with Rigaku and Bruker CCD diffractometers led to refined compositions Ba₄As₂_{5,6,0} and Ba₄As_{2,6,0} respectively. On the other hand, attempted syntheses of the (Ba,Sr)₄Sb₃ and Ca₄(Pn)₃ phases produced only other known phases (see Experimental Section).

**Structure.** The three stoichiometric A₄Bi₃ compounds A = Sr, Ba, Eu are antitypes of the Th₄P₃ structure, and the same is true for Ba₄As₂_{6,6} save for the 1/3 random vacancies...

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on the anion lattice. The structure is quite simple in local environments but complex as a whole. The divalent cations occupy the position 16c \((x, x, x)\) in which they form two enantiomeric networks (Figure 1). The Bi (As) atoms in positions 12a \((\frac{3}{8}, 0, \frac{1}{4})\) generate three condensed diamond-like networks each composed of 3-connected 6-membered rings. Note that the anionic network has no variable parameters, and thus, the interatomic distances are interrelated by the lattice constants. Furthermore, there are no direct interactions between the anions, the \(Pn-Pn\) distances being greater than 4.7 Å for the bismuthides and 4.6 Å in the arsenide. The Bi(As) atoms are coordinated by eight cations, and the cations have six \(Pn\) atoms and five cation nearest neighbors, three of the five cations having shorter distances to each other, 4.040(1) and 3.840(1) Å in \(Ba_4Bi_3\) and \(Ba_4As_{2.6}\), respectively.

**Properties.** Figure 2a shows resistivity data for a single-phase sample of \(Ba_4Bi_3\) measured by the “Q” method. The results are characteristic of a moderately poor metal, with \(\rho_{298} = 43.6 \mu\Omega\cdot\text{cm}\) and a mean temperature dependence of 0.09(1) K\(^{-1}\), the sign of the latter being taken as the defining characteristic of a metal. The magnetic susceptibility results for \(Ba_4Bi_3\) are shown in Figure 2b. Above 12 K, the data are almost temperature-independent, \(\sim 6.9 \times 10^{-4} \text{emu/mol}\) after container and ion core corrections, and the magnitudes are quite typical for Pauli-paramagnetism in such phases. The magnetic susceptibilities and electronic resistivities of \(Eu_4Bi_3\) powder were also remeasured. The magnetic results are almost the same as reported before by an effective magnetic moment of 7.5(1) \(\mu_B\), closely corresponding to the expected result for \(Eu^{2+}\). On the other hand, the electrodeless “Q” method gave \(\rho_{298} = 38.1 \mu\Omega\cdot\text{cm}\) and a mean temperature dependence of 0.30(1) K\(^{-1}\) for \(Eu_4Bi_3\). This is much more in line with the behavior of \(Ba_4Bi_3\) than the evidently erroneous result reported earlier for \(Eu_4Bi_3\), \(\rho_{298} = 1.29(1) \Omega\cdot\text{cm}\). Resistivity measurements on \(Ba_4As_{2.6}\) by the “Q” method were also attempted, but the resistivity was too large to give an answer by this method. A lower limit of 1000 \(\mu\Omega\cdot\text{cm}\) was estimated at 150 K, which is reasonable in view of the probable band gap (below).

**Band Structures.** While the structure of the \(Ae_4Pn_3\) compounds is fairly simple, the electronic structures are somewhat more difficult to rationalize. According to the Zintl–Klemm concept, it is assumed that the alkaline-earth metals are cations and donate their electrons. Accordingly, there are no \(Pn-Pn\) bonds in these compounds, a formal electron counting suggests a one-electron deficiency per formal unit for \(Ba_4Bi_3\) and \(Sr_4Bi_3\), whereas \(Ba_4As_{2.6}\) is assumed to be a Zintl phase with the appropriate substoichiometry.

The general features of the band structures of \(Sr_4Bi_3\), \(Ba_4Bi_3\), and the hypothetical \(Ba_4As_3\) are quite similar. Each consists of four distinctively different areas of bands. First are low lying “semicore” pnictogen s bands with a low degree of dispersion and bandwidth, followed by the “valence” bands composed mainly of pnictogen p orbitals around the Fermi level. The top levels of these broad band area cross \(E_F\), the Fermi level, with special steepness around \(\Gamma\). These bands also contain substantial contributions from alkaline-earth-metal p and, most important, d states, particularly for the two bismuth compounds. The alkaline-earth metal d states themselves occur in wide bands at higher energies above a gap, starting \(~1.3\) eV above the Fermi level; \(Sr/Ba\) p bands mix substantially with \(Pn\) p, and thus, they are important. The substantial density of states at the Fermi level for \(Sr_4Bi_3\) and \(Ba_4Bi_3\) indicates an open band character of the bismuth anion and explains the metallic properties of those...
compounds. The band and DOS data for the strontium member are shown in Figure 3, and Figure 4 illustrates in a fatband representation the participation of Sr 4d orbitals in the valence band. Likewise, the cation–anion covalency in Sr4Bi3 is emphasized by the COHP curve in Figure 5, and that for Ba4Bi3 is similar.

The dependence of the results on the alkaline-earth metal cation is quite clear from the calculations. The Bi valence bands in Sr4Bi3 have a higher dispersion and width than in the Ba compound in which the electrons are somewhat more localized. In other words, the stroncium cations have the larger charge potential (charge/radius ratio) and tend to polarize the “soft” bismuth anion and destabilize its anionic charge even though mixing of cation (mainly d) states into the valence band is slightly greater for barium.

On the other side, the influence of the anions in this class of compounds can be studied by a comparison with Ba4As12.67 or, better, the idealized Ba4As3 (with fully occupied anion positions) with Ba4Bi3. Most important is the change of bandwidth and dispersion upon replacement of Bi by As. The dispersion of the valence bands (which are mainly pnictogen p in character) around the Fermi level is distinctly (~16%) less in the comparable (hypothetic) arsenic analogue. This shows the general periodic tendency of lighter anions to stabilize electrons in their valence shells, whereas heavier elements tend to have more disperse, less localized valence bands, and a greater tendency to metallicity. Therefore, an open shell anion is less favorable for arsenic. The hypothetical Ba4As3 lacks one electron for a closed valence shell, and the system responds by removing 1/3 of the 12 As and four bands per cell to give just the closed shell result with disordered monoanions and vacancies.

The regularities with antimony are worth noting again; no Ae4Sb3 compounds could be isolated for Ae = Ca, Sr, Bi. Rather, principally the alternative Ae11Sb10 phases are formed instead. Antimony is clearly a better anion former than is bismuth, and it does so in other products rather than generate vacancies in this lattice or an open valence band. The regular trends we note for the series As–Sb–Bi also parallel the increase in metallic characteristics as s–p mixing diminishes and the former orbitals become more corelike. 24

Finally, the valence problems associated with Ae4Pn3 compositions in the anti-Th3P4 structure type can presumably also be expressed in ternary systems through partial substitution of lower-valent anions on that lattice or interstitially. Three examples are suggestive, but no properties are known and the compositions themselves are not entirely certain. Earlier attempts to make ternary derivatives of Mn3Si3 structures of Ca4Sb2 and Ba4Sb2 stuffed with interstitial S or I gave mixed anion varieties of (Th3P4)1− structures instead as Ca4Sb2.4S0.4 and Ba4Sb2.5I0.5. 25 The former, which has the

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**Figure 3.** Band structure and densities-of-states for Sr4Bi3 (E_F = 0).

**Figure 4.** Band structure in the fatband representation for Sr d in Sr4Bi3 in the valence band region. Note the strong d-contribution to the levels right below the Fermi level.

**Figure 5.** COHP data for Sr–Bi interactions in Sr4Bi3 as a function of energy. Positive COHP values are bonding.

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same composition as the valence compound sought, \( \text{Ca}_{5}\text{Sb}_{3}\text{S}_{0.5} \), was obtained in quantitative yield according to the Guinier powder pattern, presumably with 6.7% vacancies on the mixed anion lattice. The iodide was obtained as a mixture from a \( \text{Ba}_{5}\text{Sb}_{3}\text{I} \) composition but was later obtained in \( \sim 80\% \) yield and refined from single crystal data for the composition \( \text{Ba}_{4}\text{Sb}_{2.5}\text{I}_{0.5} \). (Distinguishing the latter two elements would be problematic). Finally, the present structure type was also found in about 80% yield, presumably as \( \text{Ba}_{4}\text{Bi}_{2.5}\text{F}_{0.5} \) (along with \( \text{Ba}_{16}\text{Sb}_{11} \) and a trace of \( \text{BaF}_{2} \)) from an attempt to prepare \( \text{Ba}_{5}\text{Sb}_{3}\text{F} \) in the orthorhombic \( \text{Ca}_{5}\text{Sb}_{3}\text{F} \) structure.\(^{25,26}\) In this case, the fluoride would presumably lie in the tetrahedral interstitial cavities in this structure type. Further studies in these areas could be profitable.

**Acknowledgment.** We are indebted to S. Budko for the magnetic susceptibility data, to L. Chi who made the first investigations of the nominal \( \text{Ba}_{4}\text{As}_{2.67} \), and to A. E. Leon-Escamilla for the earlier discovery of some of the compounds studied. A.-V.M. thanks the Alexander-von-Humboldt Foundation for a Feodor-Lynen fellowship.

**Supporting Information Available:** Tables of additional crystallographic and refinement parameters for \( \text{Ba}_{4}\text{Bi}_{3}, \text{Sr}_{4}\text{Bi}_{3}, \) and \( \text{Ba}_{4}\text{As}_{2.60} \). Figures of magnetic susceptibility and resistivity data for \( \text{Eu}_{4}\text{Bi}_{3} \). These materials are available free of charge via the Internet at http://pubs.acs.org.

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