



Wanyue Peng[†], Sviatoslav Baranets^{†,‡} and Svilen Bobev *

Department of Chemistry & Biochemistry, University of Delaware, Newark, DE 19716, USA

* Correspondence: bobev@udel.edu; Tel.: +1-302-831-8720; Fax: +1-302-831-6335

+ These authors contributed equally to this work.

‡ Current Address: Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, USA.

Abstract: Crystals of a new ternary compound in the Ca-In-As family, Ca₃InAs₃, have been successfully synthesized via flux growth techniques. This is only the third known compound between the respective elements. As elucidated by single-crystal X-ray diffraction measurements, Ca₃InAs₃ crystallizes in the orthorhombic space group *Pnma* (No. 62, Pearson symbol *oP*28) with unit cell parameters *a* = 12.296(2) Å, *b* = 4.2553(7) Å, and *c* = 13.735(2) Å. The smallest building motifs of the structure are InAs₄ tetrahedra, which are connected to one another by shared As corners, forming infinite [InAs₂As_{2/2}] chains. The latter propagate along the crystallographic *b*-axis. The As-In-As bond angles within the InAs₄ tetrahedra deviate from the ideal 109.5° value and range from 98.12(2)° to 116.53(2)°, attesting to a small distortion from the regular tetrahedral geometry. Electronic structure calculations indicate the opening of a bandgap, consistent with the expected (Ca²⁺)₃(In³⁺)(As³⁻)₃ formula breakdown based on conventional oxidation numbers. The calculations also show that the Ca–As interactions are an intermediate between covalent and ionic, while providing evidence of strong covalent features of the In–As interactions. Weak *s-p* hybridization of In states was observed, supporting the experimentally found deviation of the InAs₄ moiety from the ideal tetrahedral symmetry.

Keywords: arsenides; crystal structure; crystal growth; X-ray diffraction; Zintl phases

1. Introduction

Pnictogen-based (pnictogen, i.e., the group 15 elements P, As, Sb and Bi; abbreviated as Pn hereafter) compounds with a formula of A_3MPn_3 are reported to crystallize in several distinct structures, where A is an alkaline-earth or divalent rare-earth metal, M is a triel, i.e., a group 13 element [1]. The different structure types are originating from the way the MP_4 tetrahedra are interconnected and arranged.

For example, Ca₃AlAs₃ [2], Sr₃InP₃ [3], Ca₃InP₃ [4], Ca₃GaAs₃ [4], Ca₃AlSb₃ [5], Eu₃InAs₃ [6], and Yb₃AlSb₃ [7] all crystallize in the orthorhombic *Pnma* space group (No. 62. Pearson symbol *oP*28). The *MPn*₄ tetrahedra in the structures of the abovementioned compounds are connected to one another with shared *Pn* corners, forming an infinite straight chain along the crystallographic *b*-axis. Surveying the published structures suggests that the In-containing A_3MPn_3 compounds tend to crystallize in the *Pnma* structure described above, although this is a requisite for the realization of infinite chains as a structural motif.

One should also note that there are A_3MPn_3 structures with corner-sharing tetrahedra crystallizing in different space groups. The Sr₃GaSb₃ compound [3] is a relevant example here since the GaSb₄ tetrahedra in the structure are also connected via corner-sharing, but the resultant chains are not straight, but rather zigzagging. This difference results in an amplified structural complexity in Sr₃GaSb₃, evident from the increased number of repeating units per unit cell and the lowered symmetry; the latter compound crystallizes with the monoclinic space group $P2_1/n$ (No. 14; Pearson symbol mP56) [3].



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). In addition to corner-sharing, the tetrahedra in an A_3MPn_3 compound can also be connected via edge-sharing. Such connections are observed in Ba₃GaSb₃ (space group: *Pnma*) [4], Ba₃AlSb₃ [2] (space group: *Cmce*), and Eu₃AlAs₃ (space group: *P*2₁/*c*) [8], in which the tetrahedra are connected via *Pn*–*Pn* edge-sharing, forming $[M_2Pn_6]^{12-}$ dimers (diborane-like units of dual tetrahedra). The different space groups of the above compounds reflect the different arrangements and orientations of the $[M_2Pn_6]^{12-}$ dimers within the unit cell.

In the present study, we synthesized a previously unknown compound in the A_3MPn_3 family, Ca₃InAs₃. We determined the crystal structure of Ca₃InAs₃ via single-crystal X-ray diffraction methods. Electronic structure calculations show that the bonding between Ca–As has an admixture of covalent and ionic character, while evidence of strong covalent features of the In–As interactions is observed.

2. Materials and Methods

2.1. Synthesis

Single crystals of Ca₃InAs₃ were synthesized by using indium as molten flux. Ca, In, and As were purchased from Alfa Aesar with stated purity of 99.9 wt % or higher, and were used as received. Manipulations were carried out in an argon-filled glovebox. A starting composition of Ca:In:As of 1:30:1 was used. Excessive In was used as the medium for the crystal growth. The corresponding amounts of elements were loaded into 2 mL alumina crucibles, which were then put inside fused silica ampoules. A piece of quartz wool was placed on top of the crucible without touching the elements inside. The ampoule was sealed under a vacuum level of ca. 30 millitorrs.

All samples in this study were heated in standard muffle furnaces with a temperature profile as follows: 100 °C \rightarrow 200 °C/h to 1000 °C \rightarrow hold at 1000 °C for 15.5 h \rightarrow 5 °C/h to 650 °C. At this point of the crystal growth, the sealed tube was taken out from the furnace, flipped, and the molten metallic flux was separated from the grown crystals by centrifugation. The sealed ampoule was break-opened in the glovebox afterwards. Inspection of the specimen under an optical microscope revealed the presence of many small crystallites, the majority of which were CaIn₂As₂ [9] with only a minor fraction of crystals of Ca₃InAs₃.

The crystals were brittle and had a metallic luster; they were found to degrade in ambient air within about ten minutes. During the brief exposure, the crystals' surface becomes tarnished; after several hours in air the material becomes amorphous.

2.2. Single-Crystal X-ray Diffraction (SC-XRD)

Single-crystal X-ray diffraction (SC-XRD) was performed on single crystals using a Bruker APEX II CCD diffractometer, equipped with Mo K α radiation. Single-crystal morphologies for Ca₃InAs₃ were typically thin rod-like, but were cut (under a microscope in dry Paratone-N oil) to block shape, with each side smaller than 100 μ m in length. The measurements were conducted at a temperature of 200 K under a N₂ atmosphere to achieve optimal data quality and avoid decomposition of the sample during the measurement. Data integration and semiempirical absorption correction were performed with the Brukersupplied software [10]. The crystal structure was solved with ShelXT [11] using the intrinsic phasing method. Structure refinements were carried out using the ShelXL software, which employs full-matrix least-squares minimization on F^2 [12]. Olex2 software was used as a graphical interface [13]. Atomic coordinates of all compounds reported in this paper were standardized with the STRUCTURE TIDY program [14]. All sites were refined with anisotropic displacement parameters. The site occupation factors (SOF) were checked by freeing an individual SOF, while other variables were kept fixed. No statistically significant deviations were observed for the SOF on any of the atomic sites. Final difference Fourier map was flat and featureless. Selected crystallographic data are summarized in Table 1.

Formula	Ca ₃ InAs ₃
Formula weight (g·mol ^{−1})	459.82
Radiation, λ	Mo <i>K</i> _α , 0.71073 Å
Temperature (°C)	-70(2)
Crystal system	orthorhombic
Space group	<i>Pnma</i> (No. 62)
Z	4
a (Å)	12.296(2)
b (Å)	4.2553(7)
c (Å)	13.735(2)
$V(Å^3)$	718.7(2)
$\rho_{calc} (g \cdot cm^{-3})$	4.25
$\mu_{Mo \ K\alpha} \ (\text{cm}^{-1})$	190.1
Reflections: parameters	1151: 44
$R_1 \left[I > 2\sigma(I) \right]^a$	0.0222
R_1 (all data) ^{<i>a</i>}	0.0330
$wR_2 [I > 2\sigma(I)]^a$	0.0463
wR_2 (all data) ^{<i>a</i>}	0.0496
Largest peak; deepest hole ($e/Å^{-3}$)	0.83; -1.05

Table 1. Selected crystal data and structure refinement parameters for Ca₃InAs₃.

 $[a] R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|; wR_2 = [\sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2]]^{1/2}, \text{ where } w = 1 / [\sigma^2 F_0^2 + (0.0213 \cdot P)^2 + (0.301 \cdot P)], \text{ and } P = (F_0^2 + 2F_c^2) / 3.$

2.3. Powder X-ray Diffraction

X-ray powder diffraction patterns were collected at room temperature on a Rigaku MiniFlex powder diffractometer, using filtered Cu K α radiation. Because Ca₃InAs₃ was the minor phase, and because the experiment was carried out at ambient conditions, there was a very high background. The just a few experimentally observed peaks matched mostly with the calculated positions for CaIn₂As₂ [9] (major phase) and elemental In (left over flux).

2.4. Electronic Structure Calculations

To investigate the chemical bonding of all compositions, electronic structure calculations were performed within the local density approximation (density functional theory) using the TB-LMTO-ASA program [15]. Experimental unit cell parameters and atomic coordinates from Tables 1 and 2 were used as input parameters in the calculations. In order to satisfy the atomic sphere approximation (ASA), we employed the von-Barth-Hedin functional [16] and introduced empty spheres. The Brillouin zone was sampled by a 1000 *k*-point grid. Electronic density of states (DOS), atom-projected electronic density of states (PDOS), and crystal orbital Hamilton population (COHP) were calculated with modules in the LMTO program [17].

Table 2. Atomic coordinates and	l equivalent isotropi	c displacement parameter	s (U_{eq}) for Ca ₃ InAs ₃ .
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Atom	Wyckoff Symbol	Site Symmetry	x	y	z	U_{eq} (Å ²) ^a
As1	4 <i>c</i>	.m	0.04891(4)	1/4	0.36528(4)	0.0103(1)
As2	4 <i>c</i>	.m	0.25779(4)	1/4	0.62613(4)	0.0086(1)
As3	4 <i>c</i>	. <i>m</i>	0.60837(4)	1/4	0.61098(4)	0.0085(1)
In	4 <i>c</i>	. <i>m</i>	0.05554(3)	1/4	0.69988(3)	0.0103(2)
Ca1	4 <i>c</i>	.m	0.06164(7)	1/4	0.10532(8)	0.0104(2)
Ca2	4 <i>c</i>	.m	0.26873(7)	1/4	0.28697(8)	0.0092(2)
Ca3	4c	. <i>m</i>	0.34436(8)	1/4	0.00296(8)	0.0104(2)

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

3. Results and Discussion

3.1. Crystal Structure

To date, only two compounds have been structurally characterized for the Ca-In-As ternary phase diagram, namely $CaIn_2As_2$ [9] and $Ca_3In_2As_4$ [18]. The Ca_3InAs_3 reported in the present study is a previously unknown phase and is described in the following paragraphs for the first time.

Ca₃InAs₃ crystallizes in the orthorhombic *Pnma* space group (No. 62. Pearson symbol *oP*28) with the Ca₃InP₃ structure type (also referred to as Ca₃AlAs₃ structure type) [19]. The unit cell parameters are *a* = 12.296(2) Å, *b* = 4.2553(7) Å and *c* = 13.735(2) Å. Other relevant crystallographic parameters are tabulated in Table 1. The factional coordinates of the seven crystallographically unique atomic positions are tabulated in Table 2. All positions are of the same symmetry, *m*, with the same Wyckoff position 4*c*.

A view of the crystal structure of Ca_3InAs_3 is shown in Figure 1. As shown there, we prefer to visualize the structure as Ca^{2+} cations and In–As polyanionic sub-lattice. The InAs₄ tetrahedra are connected to one another with shared As corners, forming an infinite straight chain along the crystallographic *b*-axis.



Figure 1. (a) A schematic polyhedral representation of the orthorhombic crystal structure of Ca_3InAs_3 . (b) Distinct coordination environments for Ca1, Ca2, Ca3, As1, As2, and As3. (c) The InAs₄ tetrahedra and the way they are linked (corner-sharing of the As1 atoms). The As-In-As angles deviate from the ideal 109.5° of a regular tetrahedron. As1-In-As2, As1-In-As3, and As3-In-As2 angles measure 108.81(2)°, 116.53(2)°, and 98.12(2)°, respectively. Interatomic distances can be found in Table 3.

Selected interatomic distances obtained from the single-crystal refinements can be found listed in Table 3. The In–As distances range from 2.642 to 2.685 Å. These values match very well the metrics reported for another ternary arsenides such as Eu₃InAs₃ [6], Ba₃InAs₃ [20], CaIn₂As₂ [9], Ca₃In₂As₄ [18] and Sr₃In₂As₄ [21], among others. It should also be noted the experimentally observed bond length values are comparable to the sum of the respective single-bonded covalent radii (r_{In} and r_{As} are 1.42 Å and 1.21 Å, respectively, yielding a summation value of 2.63 Å [22], which is an indication of the strong covalent bonding nature of the In–As interactions. One may also notice that there are some Ca–As distances that are shorter than 3.0 Å; this also points at substantial covalency of these interactions since the single-bonded covalent radius of Ca is 1.74 Å [22]. Further evidence of this supposition can be found in the DOS and COHP discussions in Section 3.2.

Atoms	Distance (Å)	Atoms	Distance (Å)
In–As1 (\times 2)	2.6415(5)	As2–In	2.6853(7)
In-As2	2.6853(7)	As2–Ca1 (×2)	3.0885(8)
In-As3	2.6779(7)	As2–Ca2 (×2)	3.0845(9)
In–Ca1 (×2)	3.710(1)	As2–Ca3 (×2)	2.9945(8)
In–Ca2 (×2)	3.2600(8)	As3–In	2.6779(7)
In–Ca3 (×2)	3.655(1)	As3–Ca1 (×2)	2.984(8)
In–Ca3	3.809(1)	As3–Ca1	3.026(1)
As1–In (\times 2)	2.6415(5)	As3–Ca2 (×2)	2.9623(8)
As1–Ca1	3.574(1)	As3–Ca3	3.297(1)
As1–Ca2	2.9091(1)	Ca1–Ca2	3.565(1)
As1-Ca3	3.099(1)	Ca1–Ca3	3.750(1)
As1–Ca3 (×2)	3.1345(9)		

Table 3. Selected interatomic distances (Å) in Ca₃InAs₃. Contacts longer than 3.9 Å are not shown.

In addition, it is observed that the As-In-As bond angles within the $InAs_4$ tetrahedra deviate from the 109.5° value expected for a regular tetrahedron. Similar tetrahedral distortions are also reported for other "3-1-3" compounds [6,9,20,21].

Lastly, considering the lack of any homoatomic bonding, we can rationalize the structure and the bonding in this new ternary arsenide as a typical valence-precise compound, i.e., a Zintl phase. There are two complimentary ways to understand the electronic charge balance of Ca₃InAs₃. The first way is to simply exaggerate the ionicity of the bonding and view the formula as $[Ca^{2+}]_3[In^{3+}][As^{3-}]_3$. Considering the close electronegativities of In (χ_P 1.7) and As (χ_P 2.0) [22], assigning an oxidation number of +3 for In and –3 for As may be hard to justify. Therefore, the other way may be preferred. From the point of view of the Zintl formalism [23], the formal charge of an In atom, covalently bonded to four As atoms will be 1–. In the [InAs₂As_{2/2}] tetrahedral chain, formally [InAs₃]^{6–}, two of the As atoms at the shared-corner positions have two bonds (2*b*) and their formal charge is also 1–. The other two As atoms (terminal ones) only have one covalent bond (1*b*), and need two more valence electrons to satisfy their octets; the formal charge of 1*b*-As is thus 2–. Therefore, the formula Ca₃InAs₃ could be expressed as (Ca²⁺)₃[(In^{1–})(1*b*-As^{2–})₂(2*b*-As^{1–})].

Either the fully ionic or the bonding picture within the Zintl formalism capture the essence of the valance electron count in Ca₃InAs₃, which is expected to be an intrinsic semiconductor. The notion of semiconducting behavior is confirmed by the electronic structure calculations, presented next.

3.2. Electronic Structure

The bonding characteristics of Ca_3InAs_3 were investigated via electronic structure calculations using the LMTO program [15]. We evaluated the electronic properties of the new material with calculations employing the experimental data listed in Tables 1 and 2.

The stacked atom-projected electronic density of states (DOS) curves for Ca_3InAs_3 are shown in Figure 2a, in which a calculated bandgap of approx. 0.46 eV can be observed. This value is reconcilable with those of other ternaty indium arsenides, such as Eu_3InAs_3 and $CaIn_2As_2$ which have calculated bandgaps on the order of 0.2 and 0.5 eV [6,9]. The existence of a bandgap is in agreement with the formal electron count as discussed in the previous section. Knowing that DFT methods typically underestimate the bandgap, the actual bandgap of Ca_3InAs_3 is speculated to be larger.

The majority of the states in the conduction band are dominated by Ca *d* orbitals, with minor As and In contributions. The states close to the valence band maximum are contributed mainly by the As *p* orbitals with minor Sr and In contributions. Specifically, in the region of $-1 < E - E_F < 0$ eV, the contribution of the As *p* orbitals is most considerable. The minor overlap of Ca and As states suggest that there are some covalent features between Ca and As. Therefore, due to the incomplete electron transfer of the cation, strictly speaking, Ca₃InAs₃ does not exhibit the textbook characteristics of a Zintl phase.



Figure 2. (a) The stacked atom-projected electronic density of states (DOS) for Ca₃InAs₃. The Fermi level is taken as a reference at 0 eV and represented with a dashed line. A bandgap of 0.46 eV can be observed. (b) Calculated partial DOS of different orbitals of for Ca. (c) Calculated partial DOS of different orbitals of for In. (d) Calculated partial DOS of different orbitals of for As.

A few insights can be observed for the bonding of the InAs₄ tetrahedra. In-*p* and As-*p* states showed extensive overlapping in the range of between $-4.1 < E - E_F < -2$ eV (Figure 2c,d). This means the existence of a strong covalent feature of the In–As interactions. In addition, the In atoms show a clear separation between the *s* and *p* orbitals, indicating a weak *s*-*p* hybridization. This insight agrees well with the InAs₄ tetrahedra distortion given by the crystal refinements.

Figure 3 shows the electronic band structure of Ca_3InAs_3 in momentum space. As evident from the plot, there are no bands crossing from the valence band to the conduction band. The lowest energy separation between the top of the valence band and the bottom of the conduction band occurs at the Γ -point. This observation is suggestive of a direct bandgap semiconductor.



Figure 3. The electronic band structure of Ca₃InAs₃. The Fermi level is taken as a reference at 0 eV and represented with a dashed line. The opening of a bandgap of ca. 0.46 eV at the Γ point is suggestive of an intrinsic, direct gap semiconductor.

The crystal orbital Hamilton population curves (COHP) for the averaged selected interactions of Ca₃InAs₃ are plotted in Figure 4. Both the In–As and Ca–As interactions are optimized at the Fermi level. For the Ca–As interactions, some bonding features can still be observed above the Fermi level when $0.5 < E - E_F < 2$ eV. This indicates the possibility of electron doping on the Ca site. In contrast, In–As interactions only show antibonding features above the Fermi level.



Figure 4. The crystal orbital Hamilton population curves (COHP) for two averaged interactions in Ca₃InAs₃. The In–As interactions are optimized at the Fermi level. Ca–As interactions are almost fully optimized at the Fermi level.

4. Conclusions

With this study, we reported on the discovery of the new compound, Ca_3InAs_3 , extending the knowledge in the Ca-In-As compositional space, and expanding the variety of compounds that crystallize with this quasi 1D-structure. The bonding characteristics of Ca_3InAs_3 were studied both experimentally and computationally. We found that Ca_3InAs_3 is an intrinsic semiconductor, where the $InAs_4$ tetrahedral building units are lightly distorted. A possibility of doping on the Ca site is also suggested.

This materials system can provide promising thermoelectric material candidates and/or topological insulators, but for quality property measurements, the synthetic challenges making a phase-pure bulk sample must be resolved.

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Data Availability Statement: The corresponding crystallographic information file (CIF) for Ca₃InAs₃ has been deposited with CSD, and the data for this paper can be obtained free of charge via http: //www.ccdc.cam.ac.uk/conts/retrieving.html (accessed on 28 September 2022) (or from the CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk). Depository number is 2210325.

Conflicts of Interest: The authors declare no conflict of interest.

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