

First-principles study of structural and electronic properties of group IV arsenides with 3:4 stoichiometry

Chenghua Hu¹ and Yuan Ping Feng^{2,*}

¹College of Science, Chongqing Jiaotong University, Chongqing, China

²Department of Physics, National University of Singapore, 2 Science Drive 3, Singapore 117542

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The structural and electronic properties of four group IV arsenides with 3:4 stoichiometry, i.e., C_3As_4 , Si_3As_4 , Ge_3As_4 , and Sn_3As_4 , were systematically investigated using a first-principles method based on the density functional theory and generalized gradient approximation. It was found that all four arsenides energetically favor the pseudocubic phase which is exceptionally stable compared to other phases. C_3As_4 is predicted to be metallic, while Si_3As_4 , Ge_3As_4 , and Sn_3As_4 are semiconductors. Si_3As_4 and Sn_3As_4 should have sizable and comparable energy gaps while the band gap of Ge_3As_4 may be smaller. In addition, the β and cubic phases of Ge_3As_4 and Sn_3As_4 become softened under pressure, and the graphitic phase becomes unstable as the group IV element evolves from C to Sn.

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I. INTRODUCTION

Group IV nitrides and phosphides in stoichiometries of X_3N_4 and X_3P_4 (where $X=C, Si, Ge, Sn$) have received much interest due to their interesting properties. Si_3N_4 is known as a hard insulator¹ and it has been used in a variety of important technological applications. The high fracture toughness, hardness, and wear resistance of Si_3N_4 -based ceramics are used in cutting tools and antifriction bearings.² In electronic applications, Si_3N_4 is used as an insulating, masking, and passivating material.³ Early studies⁴⁻⁸ on C_3N_4 predicted that C_3N_4 is a superhard material which triggered enormous interest in this material.⁹ Both Ge_3N_4 and Sn_3N_4 have been known to exist for a long time, but they attracted the attention of the research community more recently,¹⁰⁻¹⁵ due to their interesting properties and potential applications. Most of group IV nitrides were found to have similar properties. They are insulators with wide band gaps. Their equilibrium structures are hexagonal in which the nitrogen atoms form mainly sp^2 hybrid with neighboring group IV atoms, except Sn_3N_4 which prefers the γ phase. In contrast, recent first-principles studies based on density functional theory¹⁶⁻²³ indicated that group IV phosphides (C_3P_4 , Si_3P_4 , Ge_3P_4 , and Sn_3P_4) have very different properties compared to the nitrides. It was found that all phosphides energetically favor the pseudocubic structure. Unlike the nitrides for which the stabilities of a few phases (α , β , and graphite) are comparable, the pseudocubic phase of the phosphides is exceptionally stable and its total energy is lower than that of the next most stable phase by at least 0.6 eV per formula unit. The calculated band structures of all these phosphides are metallic within the local density approximation (LDA), except Sn_3P_4 which has an energy gap of 0.47 eV. Similar calculations using the generalized gradient approximation (GGA) showed that C_3P_4 is metallic, Si_3P_4 and Ge_3P_4 are narrow-gap semiconductors, and Sn_3P_4 has a moderate energy gap of about 0.836 eV. It was proposed¹⁶ that electronegativity plays a dominant role in determining the properties of these compounds. Different crystal structures are preferred by the nitride and phosphide because of the different bonding preference of nitrogen and phosphorus.

Group IV arsenides, on the other hand, have received very little attention.²⁴⁻²⁶ Mead obtained room-temperature long-wavelength reflection spectra on single-crystal germanium arsenide (GeAs) which is a semiconductor.²⁴ The effect of heat treatment on the electrophysical properties of $GeAs_2$ was studied by Ygai *et al.*²⁵ Migration of SiAs under a temperature gradient was investigated by Bolte and Gruehn.²⁶ Formation of group IV arsenides in the 3:4 stoichiometry has not been explored. To further investigate the interesting trends exhibited by group IV nitrides and phosphides, and to explore the possibility of forming group IV arsenides with 3:4 stoichiometry, we carried out first-principles calculations to study the group IV arsenides, and we present here the structural and electronic properties of C_3As_4 , Si_3As_4 , Ge_3As_4 , and Sn_3As_4 . The computational details are given in the next section. The results and some discussions are presented in Sec. III, and a conclusion is given in the last section.

II. COMPUTATION DETAILS

Total-energy calculations were performed using the Vienna *ab initio* simulation package²⁷ (VASP) based on density functional theory. The projector augmented wave potentials^{28,29} were used for electron-ion interactions and the generalized gradient approximation³⁰ was used to describe the exchange-correlation functional. The electron wave functions were expanded using plane waves with a cutoff energy of 358.4 eV for C_3As_4 and about 180 eV for Si_3As_4 , Ge_3As_4 , and Sn_3As_4 . Special k points generated according to the Monkhorst-Pack scheme³¹ were used for integration over the irreducible wedge of the Brillouin zone. We used a $6 \times 6 \times 6$ k -point mesh for pseudocubic C_3As_4 ($a=4.589$ Å and $c=4.596$ Å) during geometry optimization and increased it to $8 \times 8 \times 8$ in energy calculations. A similar k -point density was used for other structures and compounds. Good convergence was achieved with this cutoff energy and number of k points. All structures were fully optimized using the conjugate gradient method until the Hellmann-Feynman forces were less than 0.01 eV/Å.

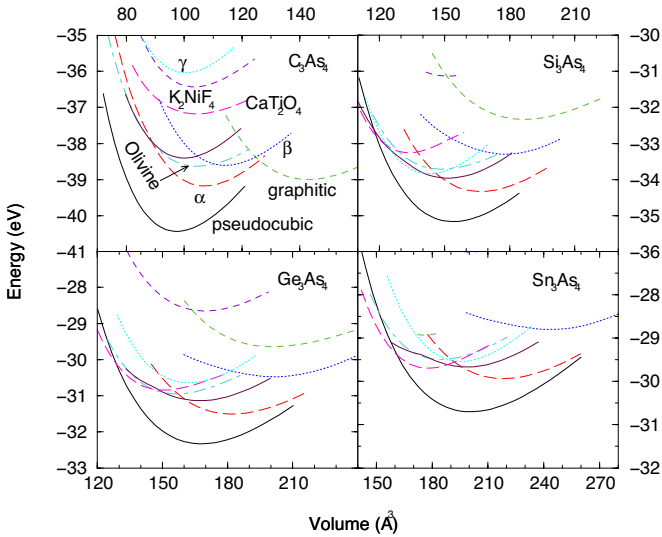


FIG. 1. (Color online) Total energy as a function of volume for various structures of group IV arsenides.

Nine crystal structures representing various crystal symmetries and bonding configurations were considered for each compound. They are α [space group $P3_1c$ (159)], β [$P6_3/m$ (143)], γ [$Fd\bar{3}m$ (227)], cubic [$I\bar{4}3d$ (220)], pseudocubic [$P\bar{4}2m$ (111)], graphitic [$P\bar{6}m2$ (187)], olivine [$Pnma$ (62)], K_2NiF_4 [$I4/mmm$ (139)], and $CaTi_2O_4$ [$Cmcm$ (63)]. Whenever possible, primitive cells were used in the calculations. Each unit cell contains two formula units (six group IV atoms and eight As atoms) for most of the crystal phases except the pseudocubic and K_2NiO_4 phases which have one formula unit per cell, and the α and olivine phases which have four formula units per cell.

III. RESULTS AND DISCUSSION

For each compound, the equilibrium cell volume was determined by calculating total energy (E) at various cell volumes (V) and then fitting the E - V data to the equation of state (see Fig. 1). For each given cell volume, the cell parameters and the atomic positions are relaxed until the total energy reaches a minimum. The total energy is then calculated at the optimized cell structure. The calculated energies per formula unit for various structures and compounds are listed in Table I. The energy is given relative to that of the pseudocubic phase in each case. The group IV arsenides were found to follow the same trend as group IV phosphides. It is known that most of the group IV nitrides energetically favor hexagonal structures in which each group IV atom is approximately tetrahedrally coordinated by nitrogen atoms and each nitrogen is planar-threefold coordinated to group IV atoms. However, the most stable phase of group IV phosphides is the pseudocubic structure which is characterized by sp^3 bonding for both phosphorus and group IV atom, and a lone pair of electrons on each phosphorus atom. For the group IV arsenides, our calculations predict that the pseudocubic phase is energetically favored relative to other phases, similar to the group IV phosphides. The stability of

TABLE I. Relative energy per formula unit of various phases of group IV arsenides.

Phase	C_3As_4	Si_3As_4	Ge_3As_4	Sn_3As_4
γ	4.39	1.33	1.65	1.16
K_2NiF_4	4.01	4.03	3.70	3.69
$CaTi_2O_4$	3.22	1.91	1.45	1.02
Cubic	2.03	1.20	1.15	1.03
Olivine	1.83	1.46	1.30	1.21
β	1.83	1.92	1.85	1.90
Graphitic	1.44	2.84	2.65	
α	1.26	0.84	0.80	0.77
Pseudocubic	0.00	0.00	0.00	0.00

the pseudocubic phase is quite exceptional. The total energy per formula unit of the pseudocubic phase is at least 0.77 eV lower than that of the next most energetically favored structure, i.e., the α phase. This is essentially due to the same reason as the exceptional stability of the pseudocubic phase of phosphides, i.e., As prefers sp^3 bonding.

The calculated volume per formula unit of the group IV arsenides in various phases are listed in Table II. It is clear that for C_3As_4 , not only is the pseudocubic phase exceptionally stable, it also has the smallest volume per C_3As_4 unit and therefore the highest density among all the phases investigated. The fact that the E - V curve of pseudocubic C_3As_4 does not intersect those of other phases in a reasonable volume range on the small volume side implies that it is impossible for pseudocubic C_3As_4 to undergo a phase transition under pressure, which is similar to C_3P_4 .¹⁷ In our calculation, a number of high-pressure phases such as the γ phase were also included. However, their equilibrium volume per C_3As_4 unit is larger and the energy per C_3As_4 unit is much higher, as shown in Fig. 1(a) and Tables I and II. Therefore, it can be concluded that for C_3As_4 , there is no pathway for phase transition from the pseudocubic phase to other structural forms under pressure. For the other group IV arsenides, phase transitions from the pseudocubic phase to other phases such as $CaTi_2O_4$ and cubic phases are possible at a moderate pressure. For example, based on the common tangent, the phase transition pressure from the pseudocubic phase to the

TABLE II. Calculated equilibrium volume per formula unit of various phases of group IV arsenides.

Phase	C_3As_4	Si_3As_4	Ge_3As_4	Sn_3As_4
γ	100.5	143.1	162.1	195.5
K_2NiF_4	103.6	151.4	169.6	200.3
$CaTi_2O_4$	104.3	133.5	150.7	177.9
Cubic	100.1	151.5	167.3	198.9
Olivine	104.4	148.7	156.6	184.6
β	114.2	178.1	201.6	243.5
Graphitic	142.9	186.5	200.4	
α	107.0	166.6	181.9	218.3
Pseudocubic	97.5	154.1	168.0	200.6

TABLE III. Structural parameters of the optimized pseudocubic phase of various group IV arsenides: lattice parameters a and c , fractional coordinates of As (u, v, w) [positions of group IV atoms are fixed by symmetry at (0,0,0) and (0.5,0,0.5)], bond length d , bond angles θ_1 (X -As- X) and θ_2 (As- X -As), where X represents a group IV atom, and calculated energy gap E_g .

Arsenide	a (Å)	c (Å)	(u, v, w)	d (Å)	θ_1 (deg)	θ_2 (deg)	E_g (eV)
C_3As_4	4.589	4.596	(0.272, 0.272, 0.228)	2.05	104.5, 104.6	105.2	<0
Si_3As_4	5.357	5.358	(0.279, 0.279, 0.222)	2.42	103.0, 103.0	103.9	0.42
Ge_3As_4	5.499	5.518	(0.282, 0.282, 0.218)	2.50	102.0, 102.2	103.3	0.16
Sn_3As_4	5.848	5.849	(0.287, 0.287, 0.213)	2.68	101.0, 101.0	102.5	0.39

$CaTi_2O_4$ phase is predicted to be 9.8 GPa for Sn_3As_4 .

As the group IV element evolves from C to Sn, a few interesting trends can be observed. First, the energy separation between a high-energy state and the ground state pseudocubic phase becomes smaller for most of the structures, and at the same time, the equilibrium volume per formula unit increases. These are mainly due to the increased atomic radius and reduced strength of interatomic interaction. The tetrahedral radii of C, Si, Ge, and Sn are 0.774, 1.173, 1.225, and 1.405 Å, respectively, and their electronegativities are 2.50, 1.41, 1.35, and 1.15, respectively, in the tetrahedrally coordinated environment.³² The increasing atomic radius and decreasing interaction strength lead to smaller cohesive energy (the VASP total energy consists of mainly cohesive energy) as the group IV elements evolves from C to Sn, and smaller differences in cohesive energies between different phases. It is also observed that Si_3As_4 and Ge_3As_4 have similar total energies and volumes. This is expected since Si and Ge have similar tetrahedral radii and electronegativities.

The graphitic structure is the most stable phase of C_3N_4 .⁴ However, graphitic C_3P_4 is less stable compared to the pseudocubic and α phases. The situation of C_3As_4 is very similar to that of C_3P_4 . Graphitic C_3As_4 has higher energy than pseudocubic- and α - C_3As_4 , and lower density than other phases. For Si_3As_4 and Ge_3As_4 , the graphitic phase becomes much less stable compared to all other phases considered in this study except the K_2NiF_4 phase. At the same time, its volume per formula unit decreases and becomes comparable to other phases. The volume decrease is a result of decreasing distance between graphitic planes due to increasing interplane interaction. Graphitic Sn_3As_4 becomes completely unstable due to increased interlayer interaction. We only managed to get a few data points near 180 Å³ for the E - V curve, and in these structures the interplane distance is reduced to approximately 2.59 Å.

It is also noted that the cubic and β phases of Ge_3As_4 and Sn_3As_4 become softened when the volume is reduced. When the volume of the unit cell is reduced to certain amount, the energy does not increase as fast as expected for further decrease in volume. Detailed structural analysis revealed that when the volume of Ge_3As_4 or Sn_3As_4 is compressed by a large amount, significant internal deformation takes place. In the case of the β phase, even though the sp^2 -bonded Ge_3As or Sn_3As unit in the a - b plane remains rigid, they rotate in the plane to accommodate the reduced volume or increased pressure. Large structural deformation was also found in cu-

bic Ge_3As_4 and Sn_3As_4 . For example, the Sn-As bond length is 2.68 Å and the Sn-As-Sn and As-Sn-As bond angles are 107.8° and 97.8°, respectively, in the equilibrium state of Sn_3As_4 . When the volume of cubic Sn_3As_4 is reduced to about 80% of the equilibrium value, the above bond length and bond angles become 2.72 Å, 95.2°, and 92.9°, respectively. It should be pointed out that these large structural deformations occurred during structural relaxation under symmetry constraints. It can be imagined that, without symmetry constraint, the cubic and β phases of Ge_3As_4 and Sn_3As_4 would easily transform to other phases.

Details of the equilibrium structural parameters of the pseudocubic phase of various group IV arsenides are given in Table III. A ball and stick diagram of the pseudocubic structure is illustrated in Fig. 2. The structure can be approximately considered as a defected zinc-blende structure, with one missing face center group IV atom (top or bottom surface in Fig. 2). Due to the missing group IV atom, the As atoms relax toward the vacant site, as can be seen by the fractional coordinates of the As atom in Table III. As a result, the bond angles X -As- X (θ_1), where X represents a group IV atom, are smaller than that in the tetrahedrally bonded structure (109.5°). In all cases, the lattice parameter c is slightly larger than a . For this reason, the bond angles θ_1 are not exactly the same. The angle involving two face center group IV atoms (such as the angle 2-3-5 in Fig. 2) is slightly smaller than that involving one face center atom and one corner atom (such as angles 1-3-2 and 1-3-5 in Fig. 2), even

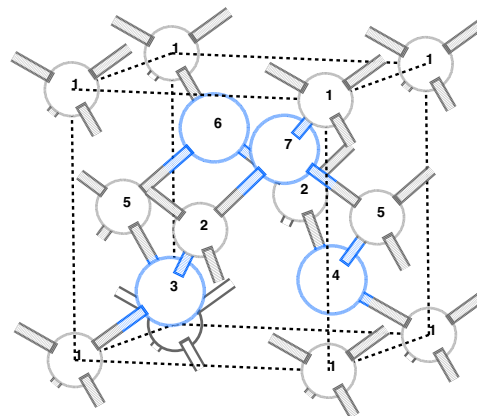


FIG. 2. (Color online) Ball and stick diagram of the pseudocubic structure. The As (group IV) atoms are shown using larger (smaller) balls. The structure is similar to a defected zinc-blende structure, with one missing face center group IV atom (top or bottom surface).

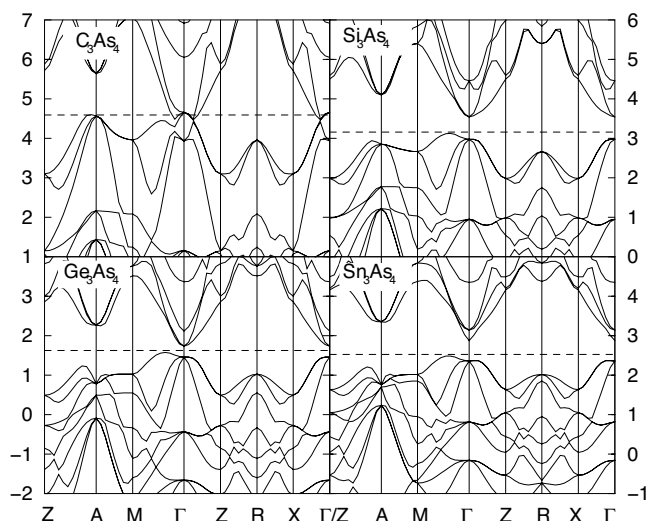


FIG. 3. Calculated band structures of the pseudocubic phase of various group IV arsenides.

though sometimes the difference is too small to be observable. The bond angles As-X-As, on the other hand, are symmetric and are the same for a given compound, but the value varies slightly between different compounds. It can be seen that degree of relaxation of the As atoms towards the vacant site increases as the group IV atom evolves from C to Sn.

We have also investigated the electronic properties of the various phases of the group IV arsenides. Most of the structures are metallic within the GGA except graphitic C_3As_4 , α -, β -, cubic, and pseudocubic Si_3As_4 , α -, graphitic, and pseudocubic Ge_3As_4 , α -, graphitic, and pseudocubic Sn_3As_4 . The calculated band structures of the pseudocubic phase of various arsenides are shown in Fig. 3. For the ground-state pseudocubic structure, C_3As_4 is metallic, while the other arsenides have a finite energy gap. However, it is known that the GGA underestimates band gap of semiconductors. Calculations based on more accurate methods such as the *GW* approximation³³ would be required to determine the energy gaps. We note, however, *GW* corrections over LDA energy gaps for related materials ranging from 0.3 to 3.3 eV (0.31 eV for CSi_2Sn_2 , 0.41 eV for CSi_2Sn_2 ,³⁴ 3.29 eV for β - C_3N_4 ,⁸ 1.7 eV for diamond, 2.0 eV for BN, 0.7 eV for BP³⁵), and the corrections are typically large for nitrides. Considering that the overlap between the lowest conduction band and the highest valence band of C_3As_4 is significant, *GW* correction of the band gap may not be able to completely remove this large overlap. Therefore, it can be concluded that C_3As_4 is metallic, or at most a narrow-gap semiconductor. The trends exhibited here by the arsenides are again similar to those of the phosphides. Earlier calculations^{18–22} showed that C_3P_4 is metallic, and Si_3P_4 , Ge_3P_4 and Sn_3P_4 are semiconductors, with energy gaps of 0.134, 0.125, and 0.836 eV, respectively, within the GGA.

It was proposed that electronegativity plays an important role in determining the electronic properties of group VI-V compounds.¹⁶ Due to the large electronegativity of nitrogen, valence electrons in C_3N_4 are attracted by and tightly bound to the nitrogen ions, leading to highly ionic bonding and a wide energy gap for C_3N_4 . On the other hand, phosphorus is

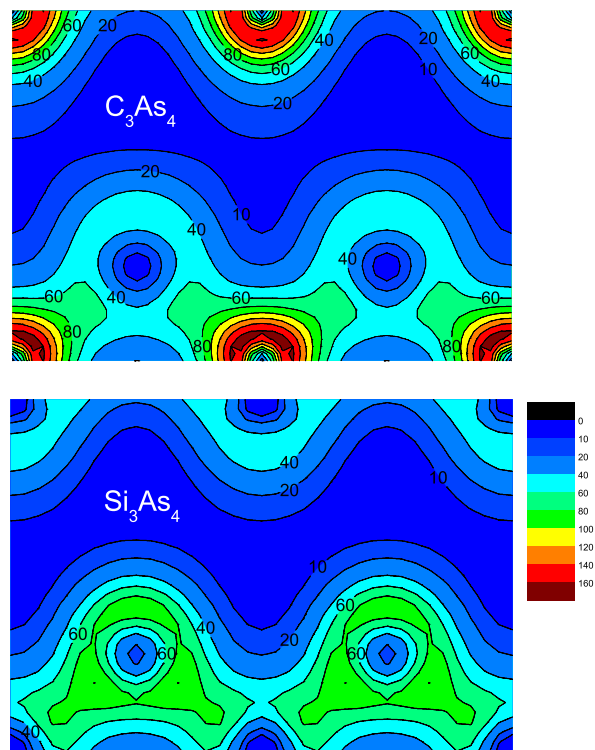


FIG. 4. (Color online) Electron density in the (101) plane of pseudocubic (a) C_3As_4 and (b) Si_3As_4 . The C or Si atoms are located at the corners and the top or bottom edge of the graph.

more willing to give away electrons to carbon in C_3P_4 due to its low electronegativity. The valence electrons in pseudocubic C_3N_4 form a covalent C-P bond, but they are more delocalized and the bonding is more metallic in nature. Since the electronegativity of arsenic (1.57) is very close to that of phosphorus (1.64),³² it is not surprising that the electronic properties of group IV arsenides are similar to those of group IV phosphides. In Figs. 4(a) and 4(b), we show the calculated electron densities of pseudocubic C_3As_4 and Si_3As_4 , respectively, using contour plots in the (101) plane. It is clear that in C_3As_4 , much of the valence electron density is concentrated around the C atoms, and those around the As atoms are generally less localized. In Si_3As_4 , the bonding between Si and As atoms is more covalent in nature, due to the comparable electronegativity between Si (1.41) and As. The electron densities in Ge_3As_4 and Sn_3As_4 are similar to that in Si_3As_4 except that the bonding in Sn_3As_4 is slightly more ionic, with a higher valence electron density around the As atoms. They are therefore not shown here. Calculated partial density of states (not shown) indicates strong *s-p* hybridization for states near the valence band edge or Fermi level in all arsenides. Therefore, it is the same mechanism which is responsible for the different electronic properties of group IV nitrides and phosphides that determines the electronic properties of group IV arsenides with 3:4 stoichiometry.

As for the group IV phosphides, the interesting structural and electronic properties of group IV arsenides with 3:4 stoichiometry can be potentially useful. These compounds crystallize in the simple pseudocubic structure which means they can be easily grown on different substrates. The exceptional

structural stability indicates that they should have very good thermal stability. These compounds offer a wide range of physical properties. Due to their similar structures, ternary and quaternary alloys based on group IV phosphides and arsenides may be formed to allow band gap engineering and tuning of their physical properties for different applications.

IV. CONCLUSION

In conclusion, using a first-principles total energy calculation, we have carried out a systematic study of the structural and electronic properties of group IV arsenides with 3:4 stoichiometry. Four compounds, C_3As_4 , Si_3As_4 , Ge_3As_4 , and Sn_3As_4 , were studied, and different possible phases were considered for each compound. It was found that all four arsenides energetically favor the pseudocubic structure,

which is exceptionally stable compared to the other phases. For C_3As_4 , our calculations predict that it is impossible for pseudocubic C_3As_4 to undergo a phase transition under pressure, which is similar to C_3P_4 . In addition, the β and cubic phases of Ge_3As_4 and Sn_3As_4 become softened at high hydrostatic pressure, which is characterized by significant internal structural deformation. As the group IV element evolves from C to Sn, increased interlayer interaction leads to an unstable graphitic phase. Our calculations predict that pseudocubic C_3As_4 is likely a metal, while pseudocubic Si_3As_4 , Ge_3As_4 , and Sn_3As_4 are semiconductors.

Due to their simple crystal structure and exceptional stability, the group IV arsenides may be potentially useful in electronic and optical devices. It would be interesting to carry out further study to investigate the structures and properties of group IV-V compounds in other stoichiometries and compare their relative stabilities.

*Electronic address: phyfyp@nus.edu.sg

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