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Ab initio engineering of materials with stacked hexagonal tin frameworks

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The group-IV tin has been hypothesized to possess intriguing electronic properties in an atom-thick hexagonal form. An attractive pathway of producing sizable 2D crystallites of tin is based on deintercalation of bulk compounds with suitable tin frameworks. Here, we have identified a new synthesizable metal distannide, NaSn_2 , with a 3D stacking of flat hexagonal layers and examined a known compound, BaSn_2 , with buckled hexagonal layers. Our *ab initio* results illustrate that despite being an exception to the 8-electron rule, NaSn_2 should form under pressures easily achievable in multi-anvil cells and remain (meta)stable under ambient conditions. Based on calculated Z_2 invariants, the predicted NaSn_2 may display topologically non-trivial behavior and the known BaSn_2 could be a strong topological insulator.

The morphology of a crystal structure reflects the underlying bonding mechanism and gives indications about material's potential applications. For instance, the high atomic density and symmetry of the sp^3 -connected framework make the diamond polymorph of carbon the hardest known bulk substance¹. The pronounced anisotropy of graphite arising from the weak van der Waals interlayer binding allows for material's intercalation with different metals and creation of excellent alkali-ion battery electrodes². The rigid, naturally hole-doped sp^2 boron backbone in magnesium diboride is responsible for the material's record critical temperature in the class of ambient-pressure phonon-mediated superconductors³. The reduced dimensionality of free-standing sp^2 frameworks of carbon determines an array of unique properties, from exceptionally high carrier mobilities⁴ to the quantum Hall effect at room temperature⁵. Making 'carbon' copies of such Nature's best structural motifs can be an effective strategy in the search for materials with even more appealing properties.

Group-IV elements are a natural choice for creating novel (meta)stable covalent networks due to the automatic fulfilment of the 8-electron rule in structures with well-defined bonding and anti-bonding states⁶. The ability of carbon to form extended sp^2 nanostructures is credited to the additional π -bonding which strengthens the hexagonal sheets. For all other tetravalent elements the diamond configuration is favored over the layered morphology. Moreover, the favorability of the sp^2 or sp^3 hybrid bonding diminishes with the element's number due to the reduction of bond integrals⁷. Consequently, tin readily transforms from the semiconducting diamond α -phase to the metallic higher-coordinated β -phase near room temperature while lead adopts the typical metallic fcc structure.

Reflective of this stability trend within group IV, graphene was the first material to be produced as a free-standing atom-thick sheet, with silicene^{8,9} and germanene¹⁰ synthesized later as single layers deposited on metallic surfaces. Zhu *et al.* have just reported on the first successful synthesis of stanene via molecular beam epitaxy on a Bi_2Te_3 substrate¹¹. The present effort to produce free-standing stanene has been inspired, in part, by the prediction of the material's behavior as a large-gap quantum spin Hall insulator induced by a strong spin-orbit coupling (SOC)¹². Due to an unwanted influence of the substrate on the material's electronic properties¹¹ and evident thermodynamic instability of 2D tin relative to the bulk phases (see Fig. 1), alternative synthesis routes need to be explored to produce desired free-standing tin-based polymorphs. Halogenation has been proposed as a possible pathway to creating stable variants of stanene while preserving its exotic electronic features^{13,14}, but 2D tin sheets are still a required precursor. Recalling that exfoliation of graphite was the original route to graphene and that sheets of germanene have been obtained through topochemical deintercalation of CaGe_2 with HCl ¹⁵, we have carried out an *ab initio* search for new synthesizable bulk compounds comprised of hexagonal tin

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Figure 1. Calculated chemical potential of Sn in known 3D, hypothetical 2D/3D, and the predicted 3D Sn-based structure. The arrows illustrate the construction of the predicted hP3-NaSn₂ out of flat hexagonal Sn layers. The superscripts show the coordination numbers for Sn atoms.

layers. In addition to being possible precursors, such compounds may display topologically non-trivial electronic properties or superconductivity observed previously in related materials comprising graphene-like layers^{3,16,17} or belonging to the Zintl family¹⁸.

Ab initio structure prediction has been playing an increasingly important role in materials development and already led to discovery of new materials^{19–21}. Successful computational strategies for identifying new synthesizable materials range from automated screening with high-throughput^{22,23} or machine learning²⁴ techniques to targeted search with unconstrained optimization^{19,25,26} or rational design²⁷ methods. The exploration of a large configurational space of structures and compositions in this study has been driven primarily by the latter, physics-based *ab initio* material engineering approach. Having established beneficial features for stability of the desired structural motif, we homed in on the Na-Sn binary system in which a new NaSn₂ phase is predicted to form under compressions as low as a few GPa as discussed on page 5, remain (meta)stable under ambient conditions, and, to the best of our knowledge, feature the first all-tin stacking of flat hexagonal layers.

A great variety of stable hexagonal layered structures - differing in the number or valence of the constituent elements as well as in the layer morphology or stacking order (see Fig. 1) - have been observed or predicted in previous studies. The AlB₂ prototype (hP3 in the Pearson notation, Fig. 2a) is the basic recurring 3-atom structure from which all the other layered variants can be derived. For example, metal diborides have been observed to have not only flat but also buckled B layers¹⁹. The known hP3-LiBC²⁸ has hexagonal nets based on B and C, the predicted²⁹ and recently observed³⁰ hP8-Li₂B₂ has an extra close-packed Li layer inserted between the B sheets, while the recently discovered hP8-Na₂MgSn has a composite Mg-Sn hexagonal layer *and* an extra Na layer³¹. BaSn₂ appears to be the only synthesized compound with zigzag Sn layers³².

Computational Methods

All our calculations were performed at the density functional theory (DFT) level with the VASP code^{33,34}. We used projector-augmented potentials³⁵ with the 4*d* electrons of Sn and 2*p* electrons of Na treated as semi-core. We chose a high energy cut-off of 500 eV and fine *k*-meshes to ensure numerical convergence of relative energies to within 1–2 meV/atom. The final results were obtained with the exchange-correlation functional parameterized by Perdue, Burke, and Ernzerhof³⁶ within the generalized gradient approximation (GGA) but we checked the sensitivity of our results to systematic errors by performing additional calculations within the local density approximation (LDA)³⁷ and the non-local van der Waals density functional optB86b³⁸. We found that SOC had an insignificant effect on relative stability. The vibrational energy contribution to the Gibbs energy calculated within the frozen phonon method^{39–41}, on the other hand, was shown to be a noticeable stabilization factor for the proposed phase. The parity analysis was carried out with QUANTUM ESPRESSO package⁴². Further technical details can be found in the Supplementary Information.

Results and Discussion

The primary goal of this study was to determine whether stable Sn-based compounds could form in the simplest hP3 configuration. As the first step, we calculated the formation energy of hP3-MA₂ compounds where A was C, Si, Ge, Sn, or Pb and M was one of 41 common metals (see Supplementary Information). According to the results of the systematic scan in Fig. S1, all the C-based compounds have positive formation energy, i.e., the smallest-size C networks do not benefit from the insertion of a metal layer. The larger tetravalent elements are seen to have islands of stability for metals with up to 5 electrons in the outer shells. For MSn₂, they are Li, Na, K, Mg, Ca, Sr, Ba, Sc, Y, La, and Zr, as seen in Fig. 3a. The negative formation energy with respect to the ground state elemental structures is a necessary but not sufficient condition for compounds' thermodynamic stability. The required construction of the convex hull under select (*P*, *T*) conditions involves a considerable effort for systems rich in complex phases. In order to narrow down our search, our next step was to analyze the importance of the electron count and the size of the added metal on the compound's stability.

Figure 2. Predicted (a) and known (b,c) binary compounds of Na (large yellow) and Sn (small grey). The charge density isosurface in (a) illustrates comparable intra- and interlayer overlaps of Sn orbitals. The 4 yellow-white spheres in (c) are Na sites with 0.5 occupancy.

Figure 3. (a) Calculated formation energies for AlB_2 -type MSn_2 compounds grouped by M 's electron count. (b,c) Variation of the a and c lattice constants in the AlB_2 -type monovalent metal stannides as a function of the alkali metal nearest neighbor distance in fcc.

Figure 4 shows the evolution of the band structure and DOS as a binary compound is assembled from single flat Sn^{2D} sheets by stacking the layers up into a Sn^{3D} framework and then intercalating it with a metal layer. The Dirac-type crossings of the p_z states at the K and H points (in blue) serve as a good marker for the relative position and population of s - p -derived bands. In an ideal case of degenerate s and p starting atomic orbitals ($\Delta E_{sp} = 0$ eV), the valence sp^2 -hybridized σ bands would have the 1:2 ratio of s and p_{xy} characters and be separated from the corresponding conduction set by a large gap. The remaining electrons would fill all the bonding π states ensuring the placement of the Dirac point exactly at the Fermi level. Even though ΔE_{sp} in all tetravalent elements is considerable (7.5 ± 1 eV⁷), the model gives an adequate description of graphene.

The orbital hybridization mechanism in Sn^{2D} is quite different. The bands in the $(-9.6, -7.4)$ eV and the $(-3.3, -1.1)$ eV ranges show little mixing and can be considered as bonding s^+ and p_{xy}^+ , respectively. The antibonding s^- states are now high enough in energy to hybridize partially with the second set of the p_{xy} states, as was discussed for stanene by Xu *et al.*¹⁴. The resulting bonding s^-p_{xy} hybrid states extend from -7.4 to just above -1.8 eV while the antibonding ones begin at -1.1 eV. The partial occupation of the latter drains electrons from the bonding p_z states and leaves the Dirac crossings about 0.4 eV above the Fermi level.

The relative band positions change considerably once the sheets are AA-stacked. The appearance of two additional neighbors only 3.11 Å away along the c -axis disperses the p_z band along the $\Gamma - A$ direction by nearly 10 eV. Interpretation of the band structure becomes more difficult because the s^- states get involved in the formation of the s^-p_z σ bonds as well [the comparable strengths of the covalent bonding within and between the layers can be seen from the charge density distribution in Fig. 2a.] The outcome of the change in bands' position and degree of mixing is the appearance of a new key feature: a deep DOS minimum at 1.3 eV above E_{Fermi} . The amount of charge

Figure 4. Calculated band structures and densities of states (DOS) without SOC for hypothetical (a,b) and predicted (c) materials with hexagonal flat frameworks: (a) a single Sn layer; (b) an AA-type stacking of Sn layers; (c) an AlB₂-type NaSn₂ compound. The size of the red, green, and blue circles is proportional to the character of the Sn *s*, *p_{xy}*, and *p_z* states, respectively. The checkered DOS area in (b) contains approximately 0.5 electrons. The full DOS bar is 2.0 states/(eV u.c. spin) for the unit cells (u.c.) containing 2, 2, and 3 atoms in (a–c), respectively.

in the checkered area needed to fill up the bonding states is close to 0.5 electron (or 1.0 e for 2 Sn atoms). Based on this analysis, monovalent metals should be particularly good candidates to stabilize the Sn^{3D} structure.

Figure 4c shows that addition of Na indeed moves the Fermi level near the bottom of the DOS minimum. The charge transfer from the Na 5s states 5 eV above E_{Fermi} does not follow the rigid band approximation. The positive potential of Na⁺ downshifts the energy of the states derived from *s* and *p_{xy}* the most because they extend farthest towards the metal site. Hence, the charge is transferred primarily onto the bonding *s*-*p_{xy}* hybrid states.

In order to see which of the alkali metals has the best chance of stabilizing the structure we examined the importance of the metal size factor. Figure 3c shows that the steady increase of the MSn₂ cell volume in the Li-Cs series masks an important irregularity occurring between K and Rb. For the larger Rb, the in-plane Sn-Sn distance shrinks but only because of the considerable expansion of the *c*-axis (see Fig. 2a). The interlayer σ bonds are effectively severed when the larger alkali atoms push the layers apart to above 5.5 Å. The loss of a major part of the 0.4-eV/atom covalent interlayer binding can be partly compensated by the layer buckling. However, a calculation of the MSn₂ relative stability with respect to the known alkali metal stannides indicated that only Na has a chance to be thermodynamically stable under near-ambient conditions.

Our next set of calculations was dedicated to the stability of hP3-NaSn₂ relative to the known ambient-pressure compounds in this binary system. The existence of mS48-NaSn₂,⁴³ a direct reference point at the 1:2 composition (Fig. 2b), simplified the task. However, we also calculated the formation energy of relevant known structures in the full Na_{*x*}Sn_{1-*x*} range to examine to which extent the compounds at nearby stoichiometries could affect the synthesizability of hP3-NaSn₂ under considered (*P*, *T*) conditions.

The Na-Sn binary system has been shown to have complex compounds some of which have been discovered in recent years^{44–46}. On the Na-rich side, the oS52-Na₉Sn₂ phase with isolated Sn polyanions and cI76-Na₃₀Sn₈ phase with isolated tin atoms are correctly reproduced as low-temperature ground states. The phases with *x* ≤ 0.5 include tI64-NaSn, tP12-NaSn₅, and oS288-Na₄₀Sn₁₀₄ phases with complex 3D Sn frameworks. The last two compounds are 7 meV and 23 meV above the tie-line indicating their possible metastability.

The most relevant for the present study compounds are located at or near the 1:2 composition and covered by the Zintl rule⁴⁶. The compound with the mP78 configuration (Fig. 2c) comprises of polyanion layers stacked up along the *c*-axis 9.0 Å apart⁴⁷. Each layer in mP78 consists of 3- or 4-fold coordinated Sn atoms, arranged in 5-member rings covalently bonded along the *b* direction to form empty channels across the *a* direction. The 4-fold coordinated Sn atoms form the backbone of the layer while the lone pairs of the 3-coordinated Sn are stabilized by their proximity to the Na cations. Partial occupation of some of the Na sites in mP78 leads to an unusual Na_{1.17}Sn₂ stoichiometry and was indeed found in our study (see Supplementary Information) to be beneficial for compound's stability: Fig. 5b shows ground states at two compositions near mP78. Removal of certain Na atoms generates mS48-NaSn₂ (Fig. 2b). This 1:2 phase is slightly metastable in our calculations at 0 K and its formation could in reality be determined by a kinetic route starting from the closely related Na_{1.17}Sn₂.

The proposed hP3-NaSn₂ is 2.3 meV/atom above mS48 but could be stabilized by several factors. Zero point energy (ZPE) alone makes it virtually degenerate with mS48 in Gibbs energy at 0 K while the vibrational entropy corrections at elevated temperatures or the *PV* enthalpic term at relatively low pressures make it the true ground state (Figs 5a,c,d and S2). The accuracy of the DFT approximations does not allow us to reliably define the (*P*, *T*) boundaries of the hP3 stability region. In the LDA, which tends to overstabilize denser structures, hP3 ($V_{\text{GGA}} = 27.1$ Å³/atom) is already more stable than mS48 ($V_{\text{GGA}} = 30.3$ Å³/atom) at 0 K (no ZPE) by 18 meV/atom. Dispersive interactions can be a factor defining the ground state not only in covalent graphitic structures⁴⁸ but also in ionic-covalent materials⁴⁹. In the case of hP3 the Sn-Sn interlayer spacing is considerably smaller

Figure 5. Calculated stability of Na-Sn compounds. (a) Formation energies calculated at 0 GPa and 0 K. (b) Relative formation enthalpies of Sn-rich compounds with respect to Sn and NaSn. The solid blue circles in (a,b) correspond to previously reported compounds found to be thermodynamically stable in our calculations. (c,d) Gibbs energy difference as a function of (P , T) illustrating stabilization of the predicted hP3-NaSn₂ over the known mS48-NaSn₂; Fig. S2 shows hP3-NaSn₂ to be thermodynamically stable with respect to *all* considered compounds at 10 GPa. Zero point energy (ZPE) is taken account only in (c,d). All energy units in the figure are eV/atom.

compared to that in mS48 and the optB86b non-local functional indeed favors the former by 5.6 meV/atom. Similar trends in relative stability are expected with respect to the closely related, more complex mP78* phases: pressure, in particular, destabilizes the whole set uniformly (see Fig. S2). Our phonon calculations show absence of imaginary modes in hP3 (see Supplementary Information).

While alkali metals appear to be the preferred intercalants for the stacked flat layers of Sn, more electron-rich metals may stabilize buckled layers. Stable structures with zigzagged Sn and Ge layers have indeed been observed in BaSn₂³² and CaGe₂¹⁵, both of the EuGe₂ type (space group number 164), which makes the closest chemical analog, SrSn₂, a promising candidate. According to our calculations, SrSn₂ misses stability by only 11 meV/atom (Fig. S3) with respect to the known hR48-SrSn₃ and oS32-Sr₃Sn₅⁵⁰. Bandstructure plots for the stable BaSn₂ and the metastable SrSn₂ phases (Figs 6 and S5), reveal that layer buckling is an alternative route to place the Fermi level near the bottom of a DOS minimum. Since the large Ba and Sr atoms push the Sn layers far apart (so that they assume the most stable single-layer zigzag configuration) it might be possible to disassemble the compounds into 2D networks completely by means of electrochemical deintercalation, thermal degassing, or other methods^{15,51,52}. Our preliminary calculations indicate that compared to the observed reaction between HCl and CaGe₂ producing 2D GeH and CaCl₂, the similar reaction between HCl and BaSn₂ would be less favorable by about 1.7 eV per MA₂ formula unit but still exothermic.

In order to investigate the potential of these bulk Sn-based materials to exhibit topologically non-trivial behavior we examined the effect of spin-orbit coupling (SOC) on their electronic features, using well-established methods for materials with inversion symmetry^{53,54}. In NaSn₂, the splitting due to this relativistic effect does separate electronic bands into two groups, albeit by only a 0.1 eV gap (see Fig. 6). Evaluating the parity eigenvalues for the valence bands in the bulk NaSn₂ structure at time-reversal invariant momenta (see Supplementary Information), we find that the Z_2 invariants are 0;(001) which indicates that the compound is ‘weakly’ topological⁵⁵. However, preliminary slab calculations reveal that creation of either Na- or Sn-terminated 001 surfaces does not result in bridging the gap with just the desired surface states: breaking the interlayer Sn-Sn bond brings additional p_z bands to the Fermi level. In BaSn₂, the SOC splits the band crossing between H and A points by 0.18 eV. The parity calculation demonstrates that this metal distannide has Z_2 invariants $\nu_0;(\nu_1\nu_2\nu_3) = 1;(001)$. Even though the band structure plot in Fig. 7 shows a zero indirect band gap the compound is not necessarily a semi-metal due to limitations of the standard DFT approximations. A non-zero bulk band gap could be observed in more accurate treatment of the excited states or obtained via doping in future studies. If a true band gap can be achieved the material will be the first strong topological insulator based on a layered Sn material.

Conclusions

Our *ab initio* calculations show that hP3-NaSn₂ should be at least metastable under ambient conditions and synthesizable in multi-anvil cells under relatively low pressures. The origin of the hP3-NaSn₂ stability can be traced to the appearance of a deep minimum in the DOS of the Sn^{3D} layered framework. Na has the suitable size and the right valence to fit into the framework and fill some of the available bonding s^-p_{xy} hybrid states. The 0.4-eV

Figure 6. Calculated band structures and densities of states (DOS) without SOC for (a) a hypothetical single zigzag Sn layer; (b) a known BaSn₂ compound with zigzag Sn layers; and (c) a hypothetical BaSn₂ compound with flat Sn layers. The color coding of state characters is the same as in Fig. 4.

Figure 7. SOC-induced separation of bands into two groups in the predicted NaSn₂ and the known BaSn₂ materials by 0.1 eV and 0.18 eV, respectively.

covalent interlayer bonding is essential for stabilization of the compound but will make it difficult to exfoliate the material. The relative position of electronic bands, defined by the c/a ratio and the presence of Na⁺ cations, is difficult to predict beforehand. The final band structure has the p_z Dirac points far away from E_{Fermi} —2.6 eV below and 5.8 eV above it. However, the successful identification of a synthesizable compound with hexagonal Sn layers gives grounds for optimism that related stable materials with different compositions, stacking orders, etc., could be derived in future studies. Based on an *ab initio* examination of bulk electronic states, the known BaSn₂ material has the potential to be a strong topological insulator. A previous systematic search for superconducting features in C, Si, Ge-based AlB₂-type compounds revealed a number of candidates materials with critical temperatures of about 10 K⁵⁶. The large gradient of the DOS near E_{Fermi} in the metallic hP3-NaSn₂ prohibits us from making a reliable estimate of the material's T_c . The widely used methods for calculating the electron-phonon coupling assume a constant DOS near E_{Fermi} which would lead to dramatic errors in this case. However, the DOS value 1.2 exactly at E_{Fermi} is higher than 1.0 state/(eV u.c. spin) in β -Sn and it would not be surprising if synthesized hP3-NaSn₂ displayed comparable superconducting properties.

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Author Contributions

A.N.K. conceived the project. J.S., C.B. and A.N.K. carried out calculations and interpreted results. J.S. and A.N.K. wrote the manuscript.

Additional Information

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