A new family of two-dimensional crystals: open-framework $T_3X$ ($T=C$, $Si$, $Ge$, $Sn$; $X=O$, $S$, $Se$, $Te$) compounds with tetrahedral bonding

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(Dated: November 19, 2018)

To accelerate development of innovative materials, their modelings and predictions with useful functionalities are of vital importance. Here, based on a recently developed crystal structure prediction method, we find a new family of stable two-dimensional crystals with an open-channel tetrahedral bonding network, rendering a potential for electronic and energy applications. The proposed structural prototype with a space group of Cmme hosts at least thirteen different $T_3X$ compounds with group IV ($T=C$, $Si$, $Ge$, $Sn$) and VI ($X=O$, $S$, $Se$, $Te$) elements. Moreover, the proposed materials display diverse electronic properties ranging from direct band gap semiconductor to topological insulator at their pristine forms, which are further tunable by mechanical strain.

I. INTRODUCTION

Two-dimensional (2D) materials with a-few-atom thickness show interesting physical properties and offer great potentials for various applications. After successful exfoliation of single layers from several layered materials [1, 2], tremendous efforts have been devoted to discover novel 2D materials because new functionalities and enhanced performance may be expected in new materials and their heterostructures. Alongside experimental progress in isolating new 2D crystals, materials discovery via high-throughput computations or predictive computational methods has also been actively pursued [3–6].

Despite those recent efforts, however, database size of the 2D materials is still limited compared to that of the three-dimensional (3D) materials. In addition, significant portion of the 2D materials registered in the materials data repositories are categorized by several prototypes such as iron oxychloride, molybdenum disulfide and cadmium iodide. For instance, one 2D materials database (C2DB - http://c2db.fysik.dtu.dk) shows that the above three categories take up over half of the total items registered, and they reach even to $\sim$60% among the stable ones [3]. On one hand, generation of the database could be biased because the data were generated by decorating known prototypical structures with stoichiometric elements, indicating that chemical space was not uniformly sampled. On the other hand, it also means that crystal structure prediction (CSP), offering new 2D prototypes for a number of novel materials, can play important role to expand both material and property spaces.

Global optimization such as evolutionary algorithm [7] and particle swarm optimization [8] is a useful method to predict new crystal structures, making advances to expand 3D material space [9, 10]. Even though it works fairly well with condensed bulk materials (e.g., high-pressure phases) low-dimensional materials with reduced densities such as porous media and layered materials are difficult to be found due to the enormously expanded search space. This can be understood by an analogy of CSP to the number of combinatorial ways to arrange $m$ identical atoms in a fixed-volume unit cell containing the $n$ grids [10], i.e., $\frac{n!}{m!(n-m)!}$. Increasing $n$ for a given $m$, which is the case for low-dimensional materials, exponentially increases the number of possible configurations.

Recently, we developed a new CSP method particularly suited for 2D systems [11]: Search by Ab initio Novel Design via Wyckoff positions Iteration in Conformational Hypersurface (SANDWICH). In a new method, the 2D crystals are constructed by joining both top and bottom surface layers while the space between the surface layers is filled with bridge atoms [11]. The inner part is constructed by exhaustive enumeration of a subset of the Wyckoff positions corresponding to the space group determined by the surface layers. Our method has a merit over the conventional method in finding new 2D crystals with a stable open-framework of crystal lattice since the global optimization with a single element hardly find a hollow structure without a priori inputs from experiments [12]. Using the new method, we can generate a series of novel stable 2D silicon crystals with a large hollow channel as well as with an atomically flat surface showing interesting electronic structures [11].

In this paper, we find theoretically a prototypical 2D crystal family which can host various $T_3X$ compounds, where $T$ and $X$ stand for group IV ($C$, $Si$, $Ge$, $Sn$) and group VI ($O$, $S$, $Se$, $Te$) elements, respectively. The newly found 2D materials show an atomic arrangement with a space group of Cmme (No. 67), which is very distinctive compared with any other known 2D materials, and features an open-framework owing to strong covalent bonding characters of group IV elements. We confirmed that monolayer $T_3X$s are robust against thermal fluctuation within ab initio molecular dynamics simulations at an elevated temperature. We also find that their layered bulk forms remain stable as well with favorable binding energies moderate enough to be mechanically exfoliated. In particular, the electronic properties vary significantly in a wide range, depending on their chemical compositions, which are further shown to be tunable by mechanical strain.

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II. COMPUTATIONAL DETAILS

We found a new family of T₃Xs using our approach that was previously used to predict a series of 2D Si crystals. It is shown that one of the new 2D Si crystals with oxidized surfaces is extraordinary stable and has a direct band gap [11]. By using the oxidized atomic structure, we generated other 2D materials by substituting Si and O with other elements having the same valence electron configurations: group IV (carbon group or tetragen) and group VI (oxygen group or chalcogen), respectively. Following a nomenclature for other 2D systems such as graphene, phosphorene and MXene, we name the new series of 2D tetragen-chalcogen T₃X compounds as TXene.

The generated structures of TXenes were optimized by conjugate gradient method until the Hellmann–Feynman force on each of the atoms becomes smaller than 1 meV/Å. Total energy and forces were obtained by performing density functional theory calculations as implemented in Vienna Ab initio Software Package [13] [14] code. For structural optimization, Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional was used [15], while hybrid functional (HSE06) [16] was used for electronic structures. Spin-orbit interaction was switched on for systems with inverted bands at Fermi level. Kinetic energy cutoff of 500 eV was used for plane-wave expansion, and projector augmented wave method was used for atom cores [17]. Electron density for a given system was regarded to be self-consistent if change of both each eigenvalue and total energy compared to the previous step is smaller than 10⁻⁸ eV.

To confirm dynamical stability, we also computed phonon dispersions of T₃X by using frozen phonon method [18] as implemented in phonopy [19] code. Super-cells with a size of 3×3×1 were used to compute phonon dispersions. When computing interlayer binding energy ($E_b$), van der Waals nonlocal functionals of rVV10 were used [20].

$$E_b = \frac{E_{\text{bulk}}}{A_{\text{bulk}}} - \frac{E_{\text{monc}}}{A_{\text{mono}}},$$

where E and A refer to total energy and area of the unit-cell, respectively.

III. RESULTS AND DISCUSSION

Atomic arrangements of TXene along with typical 2D materials such as TMD and MXene are shown in Fig. [1](a). Although 1H phase of TMD and 2H of MXene are selectively shown for their structural simplicity, other phases in either TMD or MXene also show similar structural features to be discussed. TXene shows tetrahedral bonding network which is distinct from other 2D materials containing transition metal elements which prefer closed-packing. This can be confirmed by higher space groups of TMD and MXene such as P6₃m2 (No. 187) and P3m1 (No. 164), respectively, while TXene is characterized as Cmme (No. 67). In addition, thanks to strongly directional bonds of carbon group elements, open-channel structure is formed along an in-plane crystallographic orientation marked as $\hat{x}$ in Fig. [1](a). Considering the unique stoichiometry and space group of TXene, we carefully examine a number of recently reported 2D crystals and their database [8] and confirm that the present atomic arrangement of TXene is unique, and has not been reported previously elsewhere to the best of our knowledge.

The fact that TXene possesses open-framework renders a potential for energy applications for conversion and storage. Densities of monolayer TXene materials are significantly smaller than that of TMD and MXene as in Fig. [1](b), enhancing higher energy and power density for a given number of active sites. For instance, density of Sn₃S₄ is over two- and threefold reduced compared to that of MoS₂ and WSe₂, respectively, of which atomic weights of the constituent elements are comparable to each other. Furthermore, Fig. [1](c) indicates that those pores are large enough so that they could accommodate light metal ions such as lithium and magnesium, indicating that the pore array may serve as adsorption site or conducting channel for those ions. Simple estimation shows that the smaller pore radius of Si₃O (≈0 Å [21]) is greater than the radius of lithium (0.76 Å [21]) and covalent radius of silicon of 1.11 Å. Interestingly, shape of the pores varies from elliptical to circular as size of the chalcogen elements becomes greater as in Fig. [1](c).

The tetrahedral bonding network in TXene not only becomes a unique structural feature, but also stabilizes the structure. This can be confirmed by stable formation energies ($E_{\text{form}}$) in convex Hull diagram (Fig. [2](a)) for oxide systems, i.e., C₃O, Si₃O, Ge₃O and Sn₃O. Except C₃O, all the others have negative Hull distances, indicating that those systems are thermodynamic ground states at an oxygen fraction of 0.25. In case of C₃O, the positive Hull distance is attributed to exceptional stability of graphene which is even more stable than its bulk phase (i.e., diamond) at ambient condition, while it is not the case for silicene, germanene or stanene. Furthermore, in spite of the positive value, the Hull distance for C₃O is as low as 0.28 eV/atom, which could possibly be overcome and will make the C₃O a metastable phase only if the energy barrier for phase transition is high enough.

Most of the T₃X form stable layered bulk phase, and their binding energies, ranging from 5 to 33 meV/Å², fall into the easily exfoliable category defined by Mounet et al. [6] as in Fig. [2](b). Even the highest binding energy of 42 meV/Å² for Ge₃O seems very likely to be exfoliable, which is close to the threshold value of 35 meV/Å².

Some of the TXenes with Si atoms (i.e., Si₃S, Si₃Se and Si₃Te) show negative binding energies, but we confirmed that their freestanding monolayer form still shows stable phonon spectra (see Figure S1). The negative binding energy is attributed to the enlarged unit cell area when forming bulk since the binding energy is normalized by
FIG. 1. Structural features: (a) atomic arrangements of transition metal dichalcogenide (TMD), transition metal carbide (MXene) and tridecahedral chalcogenide (TXene). For TXene, size of the atoms were modified for clarity; (b) densities of various monolayers in TMD, MXene and TXene. Structural parameters for TMD and MXene are from refs. 22 and 29. (c) Poresizes of TXene for various compositions. Red and blue symbols are for $d_1$ and $d_2$ as marked in (a), and gray circle is the average values.

its unit cell area as in (1).

Freestanding monolayers of TXene represents considerable robustness against thermal fluctuations, which is confirmed by both harmonic phonon dispersion and ab initio molecular dynamics in canonical ensemble; see Figs. 2(c) and (d). Particularly, it is quite remarkable that the crystal structure of Si$_3$O remain stable even at elevated temperature of 1500 K for 10 ps, confirming the strong structural stability of the material beyond harmonic limit.

We also note that relative atomic sizes between tridecahedral and chalcogen may play an important role to determine the stability of the crystals. For instance, comparatively large chalcogen elements such as S, Se and Te bound to small carbon atoms make the corresponding compounds of C$_x$S, C$_x$Se and C$_x$Te dynamically unstable making phonon dispersion spectra have imaginary phonon modes. In addition, for Si$_3$X with X=S, Se and Te, although their phonons are stable in monolayer, their binding energies are negative as seen in Fig. 2(c), indicating that monolayer is more stable compared to the layered bulk phase. Similarly, Sn$_3$O layers do not form layered bulk structure, and they make chemical bonds with each other. The Sn$_3$O becomes dynamically unstable after forming the 3D bulk crystal. The instability is originated from the considerable interlayer interactions between Sn atoms in adjacent layers, preventing Sn$_3$O compound from forming layered structure.

Various T$_3$X compounds show versatile electronic properties. As seen in Fig. 3(a), not only that they have a variety of electronic phases such as indirect or direct band gap semiconductors and topologically non-trivial quantum spin Hall insulators with spin-orbit gaps, but also that their energy gaps vary significantly for different compositions. The computed band gap size can be as large as 3.3 eV for C$_3$O (indirect band gap), and is decreased down to 0.2 eV for Ge$_3$Se (direct band gap) for band insulators. The spin-orbit gaps range from 14 meV/Å$^2$ for Sn$_3$Te to 165 meV for Sn$_3$Se at their pristine form without mechanical strain or chemical decorations is remarkable because it is well above the room temperature thermal fluctuations (~25 meV), and comparable to other theoretically predicted materials ranging 0.1–0.3 eV, 21-27.

The band gap sizes vary differently with respect to atomic sizes, indicating different band gap opening mechanisms for band and topological insulators. For band insulators, band gap becomes diminished with larger ions, but the trend is opposite for quantum spin Hall insulators as can be seen in Fig. 3(a). This is because each of the TXene materials has the identical atomic arrangement and electron filling due to the same valence electronic configurations, but their primary bonding strength is determining the band gap size vary gradually with their sizes; the smaller the sizes, the stronger the interactions.
Versatile electronic phases and sizable band gaps in various TMDs were explained similarly [28]. We confirm this from the calculated electronic band dispersions as in Fig. 3(b); the bands marked as red arrows in various TXenes have similar charge density distributions as seen in Fig. 3(c), and their relative energetic positions vary with elements. Note that energetic position of this band plays a critical role, so that we indicate it as $\varepsilon_\Gamma^*$ for further discussion. The band is mainly composed of $p_y$ and $p_z$ orbital of the surface atoms, and shows antibonding character. Thus, $\varepsilon_\Gamma^*$ goes down with decreasing interactions or increasing size.

Fig. 3(d) shows schematic depictions accounting for various electronic structures of TXene. To begin with $\text{C}_3\text{O}$ with the strongest interactions, the $\varepsilon_\Gamma^*$ is located higher than other bands in the Brillouin zone in Fig. 3(b), making it an indirect band gap semiconductor. On the other hand, bonding in $\text{Si}_3\text{O}$ is weaker than that of $\text{C}_3\text{O}$ and the $\varepsilon_\Gamma^*$ is shifted down to make the system a direct band gap semiconductor. Note that $\varepsilon_\Gamma^*$ seems to vary the most sensitively to the interaction strength compared to the conduction bands with different momenta. Further decrease of interaction strength make the $\varepsilon_\Gamma^*$ continue to be decreased, and eventually make the two band edges near the Fermi level inverted with respect to each other, realizing quantum spin Hall insulator; see Fig. 3(b) and (d). Thanks to presence of inversion symmetry, we confirmed the $Z_2$ topological invariant of the systems with band inversion to be 1, identifying those inverted bands topologically nontrivial.

It is worth noting here that prediction of a robust structural template that can host various chemical compositions will help accelerate discovery of novel materials in many ways. Firstly, a series of novel materials sharing the same atomic arrangement but with different interaction strength will display a variety of properties, e.g., electronic properties in Fig. 3(a), thus extending property spectra by exploring material space. Furthermore, the predicted structural prototype can also be used to further find novel materials by performing high-throughput calculations, which can expand elements for substitution to a variety of elements in the periodic table. The 2D CSP method used in this work (SANDWICH [11]) is highly efficient and transferable, and is anticipated to be used to uncover other 2D structural prototypes which have not been explored yet. Lastly, the rich variety of materials database containing novel materials with wide ranges of structure-property relations can be used for predictive models based on machine learning and artificial intelligence.

The diverse electronic properties, previously shown to be controlled primarily by bonding strength of the surface atoms, can be tuned further by mechanical strain. In particular, we show the effects of uniaxial strain along $\hat{x}$ ($\epsilon_{xx}$) which is along the zigzag chain of tetragen atoms on the surface as seen in Fig. 3(a). It is confirmed that not only energetic gaps change quantitatively according to the uniform mechanical strain on the system, electronic phases of individual $\text{T}_3\text{X}$ systems may also be altered qualitatively as well. As discussed previously, the $\epsilon_\Gamma^*$ plays a crucial role to determine the electronic property. Therefore, we examine the relative positions of $\epsilon_\Gamma^*$ and $\epsilon_\Gamma^*_{\!\text{xx}}$ (the empty band at momentum of $\Gamma$) with respect to the valence band maximum. For instance, $\Delta_\Gamma$ is defined as energy difference between $\epsilon_\Gamma^*$ and the valence band maximum. In all the cases, the $\Delta_\Gamma$ decreases with positively increasing $\epsilon_{xx}$, while the $\Delta_\Gamma$ responds oppositely as in Fig. 3. Thus, for positive uniaxial strain along the $\hat{x}$-axis, there is a crossover between $\epsilon_\Gamma^*$ and $\epsilon_\Gamma^*_{\!\text{xx}}$ at $\epsilon_{xx}$ of ~4% (marked as arrow) showing indirect-to-direct band gap transition for $\text{C}_3\text{O}$. Similarly, $\text{Si}_3\text{Se}$, a small direct band gap semiconductor, becomes a quantum spin Hall insulator when it is slightly elongated along the surface chains, while it remains a direct band gap semiconductor otherwise. The negative $\epsilon_{xx}$ at around -3.5 makes the system have indirect band gap in Fig. 3(b).

### IV. CONCLUSION

In conclusion, we demonstrate theoretical prediction of a structural prototype for a new family of 2D crystals, $\text{T}_3\text{X}$, or TXene, composed of group IV (T) and group VI (X) elements with tetrahedral bonding network as well as open-framework. We confirmed 13 stable monolayers of 2D $\text{T}_3\text{X}$ compounds, and most of them also formed stable layered bulk phase with their binding energies falling in desired range. In particular, a significant thermal stability was confirmed for Si$_3$O monolayer by ab initio...
molecular dynamics simulations at elevated temperature.

Moreover, the $T_3X$ compounds show versatile electronic structures, which is mainly due to the varying interaction strengths, which are tunable by mechanical strain. The novel 2D structural prototype with a number of stable compounds already found and more to be found potentially may not only demonstrate intriguing material properties, but also accelerate novel materials discovery.

ACKNOWLEDGMENTS

We thank Korea Institute for Advanced Study for providing computing resources (KIAS Center for Advanced Computation Linux Cluster System) for this work. Y.-W.S. was supported by NRF of Korea (Grant No. 2017R1A5A1014862, SRC program: vdWMRC Center).

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SI. PHONON SPECTRA FOR SILICON COMPOUNDS

FIG. S1. Phonon dispersion and density of states for (a) Si₃S, (b) Si₃Se and (c) Si₃Te.