Screening 0D materials for 2D nanoelectronics applications

Mohammad Bagheri  Hannu-Pekka Komsa*

M. Bagheri, Prof. H.-P. Komsa
Microelectronics Research Unit, University of Oulu, P.O. Box 8000, 90014 Oulu, Finland
Email Address: hannu-peeka.komsa@oulu.fi

Keywords: 0D materials, database screening, density-functional theory, nanoelectronics

As nanoelectronic devices based on two-dimensional (2D) materials are moving towards maturity, optimization of the properties of the active 2D material must be accompanied by equal attention to optimizing the properties of and the interfaces to the other materials around it, such as electrodes, gate dielectrics, and the substrate. While these are usually either 2D or 3D materials, recently K. Liu et al. [Nat. Electron. 4, 906 (2021)] reported on the use of zero-dimensional (0D) material, consisting of vdW-bonded Sb$_2$O$_3$ clusters, as a highly promising insulating substrate and gate dielectric. Here, we report on computational screening study to find promising 0D materials for use in nanoelectronics applications, in conjunction with 2D materials in particular. By combining a database and literature searches, we found 16 materials belonging to 6 structural prototypes with high melting points and high band gaps, and a range of static dielectric constants. We carried out additional first-principles calculations to evaluate selected technologically relevant material properties, and confirmed that all these materials are van der Waals-bonded, thus allowing for facile separation of 0D clusters from the 3D host and also weakly perturbing the electronic properties of the 2D material after deposition.

1 Introduction

Two-dimensional (2D) materials are widely investigated for use in nanoelectronics devices, especially as an ultrathin channel in next-generation field-effect transistors and novel logic architectures [1, 2, 3], memory cells [4, 5], memristors [6, 7], rectenna [8], and others [9]. In all of these applications, one needs to optimize not only the properties of the “active” 2D material, but also all the other materials around it, such as the dielectrics, electrodes, and substrate, and the material interfaces between them. In a wide majority of cases, either other 2D materials or common 3D materials are used for these purposes. Recently, formation of 2D molecular crystal was demonstrated from Sb$_2$O$_3$ 0D material, i.e., a material consisting of weakly bound small molecular units with no dangling bonds [10]. Using these as a substrate or gate dielectric in 2D material field-effect transistors resulted in high mobility, small hysteresis, low density of trap states, and high subthreshold slope [11]. The authors called for theoretical studies to find more suitable 0D material candidates [11, 12].

While 2D and 1D materials have been searched in many previous publications by screening experimental and/or computational material databases [13, 14, 15, 16], to the best of our knowledge, not 0D materials. While 0D materials are easily identified using the same dimensionality identification methods, many of the found materials are crystalline phases of substances that are gaseous or liquid even in atmospheric conditions, and thus not useable in the above-mentioned applications. Finding the materials that are crystalline at technologically relevant temperatures requires estimating the melting points, which is computationally highly demanding.

In this Letter, we take first steps in identifying a set of promising 0D materials for use in electronics applications, as a substrate or as a gate dielectric. We achieve this by combining screening of the Materials Project database and supplementing it by manual pruning of the list, most importantly by extracting experimental melting points from the literature. We identified 16 materials belonging to 6 structural prototypes with high melting points and high band gaps, and both high and low dielectric constants. We performed van der Waals density-functional theory calculations to evaluate selected material properties and also studied their interaction with the prototypical 2D material MoS$_2$.

2 Results

2.1 Database screening

We start by performing a database search to Materials Project (MP) [17], as illustrated in Fig. [1](a), with the following search criteria
Cr1 The structure is classified to have 0D dimensionality.
Cr2 The structure consists of only one type of 0D cluster and the size of the cluster is larger than 3 atoms.
Cr3 Energy above convex hull \( E_{\text{hull}} \) is less than 0.1 eV/atom.
Cr4 The MP entry contains calculated dielectric constant.

Several approaches have been proposed for the classification of structure dimensionality [18, 14, 19]. We are using the algorithm proposed by Larsen et al. [19], which also gives a useful measure of the degree of “0D-ness”. Upon applying Cr1, out of 126335 materials in MP (accessed on 25th Jan 2022), 8335 were identified as 0D materials.

Criterion Cr2 is chosen for simplicity and since deposition of materials consisting of many different clusters can be difficult to control, especially since the deposition is ideally carried out at a relatively low temperature. The clusters are compared only by the formula (number and types of atoms in the cluster), not their atomic structures. Application of this criterion (on top of Cr1) yields 2395 materials. In addition, we have required that the number of atoms in the cluster is larger than 3. Clusters with one atom can be trivially ignored (mostly noble gases), and most systems with 2- or 3-atom clusters correspond to solid phases of, e.g., hydrogen halides (HF, HCl, etc.) or simple molecules such as \( \text{N}_2 \), \( \text{H}_2\text{O} \), and \( \text{CO}_2 \). It is unlikely that very promising new 0D materials can be found among these. Finally, we have required that the “0D-ness” dimensionality score used in the classification scheme is higher than 0.8 [19]. The threshold was found by manually inspecting the structures with lowest score and comparing the dimensionality to that reported in MP. The materials with low dimensionality score are borderline between different dimensionalities and usually indicates that the bonding between the (nearly) 0D clusters is stronger than in purely vdW-bonded systems. Application of these criteria yields 1965 materials.
Applying the energy criterion Cr3, reduces the number of material candidates by about a factor of two to 942. Finally, in the last step of our database screening, criterion Cr4 yields a marked reduction in the number of entries, down to 162. These materials are listed in Table S1. Omitting such a large number of entries (780) may appear unwarranted, but we will revisit this group of materials later in this paper. In the next stage, we manually pruned the list. First, if several phases of same material are found, we retain only the lowest energy phase, down to 138 materials. Inspection of the list also indicates that many of these materials are liquid or gaseous under atmospheric conditions (e.g., methane, ammonia, and various acids). In order to find materials with stable crystalline structure at moderate processing temperatures, we collected experimentally measured melting points for all materials where we could find one (also listed in Table S1). After removing the materials that are known to be liquid or gas under typical operating temperatures (melting point below 100 °C), we are left with 56 entries. The band gaps with respect to rotationally averaged static dielectric constants, or “polycrystalline dielectric constant”, ε\text{poly}, for these 56 materials are plotted in Fig. 1(b). In electronics applications with relatively slowly varying fields, the static dielectric constants are more relevant than the high-frequency one ε∞. In fact, the ionic contribution to the dielectric constant is critical for achieving large screening, as evidenced from the plot of the band gap vs. ε∞ shown in Figure S1.

In order to find materials suitable for use as gate dielectrics, we extract materials with band gap larger than 2 eV and ε\text{poly} larger than 5. The relatively low band-gap threshold was chosen since DFT with semilocal functionals underestimates gaps, sometimes significantly so, by up to a factor of two. In this group, shown in Fig. 1(b), there are only 13 materials, which we analyze in detail. The atomic structures of the corresponding 0D clusters are shown in Fig. S2 (and in Fig. 2 for the promising candidates). The only material with very high melting point (mp.) is Sb2O3 (656 °C), that was already previously identified [10, 11]. The atomic structure consists of Sb3O6 cages, similar to C10H16 carbon cages, called adamantane, but without terminating H. There are few materials with higher dielectric constant, such as HgBr, HgCl, and Re2H4O9, but those have also lower band gap and lower melting point. Moreover, although HgBr and HgCl have fairly high mp., they are unfortunately highly toxic. Re2H4O9 structure is similar to, but not exactly the same as, that of perrhenic acid. It is a metal oxide coordinated with water with mp. of 115 °C, which is likely too low.

Among others (from high to low band gap), PH4NF5 is a Lewis acid-base adduct, with fairly little experimental data. It has been synthesized, but expected to have low melting point [20]. BH2N has a low mp. of 104 °C. No mp. was found for Te2H2O3F4, but stable at room temperature and computationally stable. H4CSN2, thiourea, has mp. of 182 °C, making it possibly interesting. HIO3, iodic acid, has band gap and dielectric constant close to Sb2O3, but the mp. of 110 °C is again low. GaHgCl4 has been synthesized and is computationally stable. No mp. was found and it is sensitive to humidity [21]. CoH8(BrO2)2 (or CoBr2(H2O)4) consist of hydrated CoBr2 molecules. The degree of hydration is sensitive to temperature between 0-100 °C, which may prove problematic in applications. We could not find mp., but high E\text{hull} of 0.053 eV/atom suggests poor stability. Te(HO)6, telluric acid, has mp. of 136 °C, which is likely too low. Finally, As4S5 is a rare mineral called uzonite [22]. It is related to another mineral As4S4, realgar, also with fairly similar cage-like structure, and mp. 320 of °C. Thus, although the band gap and dielectric constant are fairly low, the cage-like structure and stability of arsenic sulfides makes them promising.

Eventually, the number of viable candidates found by this screening is small. In addition to Sb2O3, there are only As4S5 (and maybe very similar As4S4) (uzonite/realgar). The commonness of thiourea could make it interesting in some cases. For use as a substrate, the band gap is often more important than the dielectric constant. Low dielectric constant materials (low-κ dielectrics) are also used in separating the interconnects in circuits, to reduce crosstalk and parasitic capacitance. Moreover, in optoelectronic applications low dielectric constant might be desired in order to minimize screening by the substrate and to avoid subsequent renormalization of fundamental band gap and/or reduction in exciton binding energy [24, 25, 26, 27]. We next focus on the large band gap (> 3.5 eV) but small dielectric constant materials ε\text{poly} < 5, which yields 14 materi-
Als shown in Figure 1(d) and the structures in Fig. S3. Two interesting candidates can be immediately pinpointed: As$_2$O$_3$ and P$_2$O$_5$. As$_2$O$_3$ has the same structure as Sb$_2$O$_3$, i.e., belonging to adamantanes. It has mp. of 312 °C and is also found as a mineral arsenolite (and in small quantities in arsenic sulfide minerals uzonite and realgar mentioned above). P$_2$O$_5$ is also reminiscent of adamantanes but with additional terminating oxo groups. It has mp. 340 °C, and while this polymorph consisting of P$_4$O$_{10}$ molecules is in principle metastable, it is nevertheless commonly encountered. We note that P$_2$S$_2$O$_3$ consists of P$_4$O$_6$S$_4$ clusters similar to P$_2$O$_5$ but the tip O replaced by S. However, it has much lower mp. of 102 °C.

Highest band gaps are found from silicon clusters. SiH$_6$(NF$_2$)$_2$ is an adduct of SiF$_4$ and 2NH$_3$ and computationally stable, although mp. of only 166 °C. Si$_2$H$_2$O$_2$ and Si$_2$Cl$_2$O$_3$ cluster both have pyramidal structure consisting of four formula units, similar to P$_4$O$_{10}$. We did not find mp., but $E_{\text{hull}} = 0.023$ and $E_{\text{hull}} = 0.026$ eV/atom, respectively, suggests fairly poor stability. Highest dielectric constants are found from metal halogen compounds. FeH$_8$(BrO$_2$)$_2$ has a structure similar to CoH$_8$(BrO$_2$)$_2$ [28], and is similarly sensitive to humidity and exhibits fairly poor stability with $E_{\text{hull}} = 0.026$ meV/atom. MgH$_8$(ClO$_6$)$_2$ (or Mg(ClO$_4$)$_2$(H$_2$O)$_4$) is a hydrated version of magnesium perchlorate, which is a strong drying agent, which may again prove problematic. On the other hand, it has fairly high mp. of 251 °C and computational stability.

Otherwise, B(HO)$_3$, boric acid, has mp. 171 °C, and is also found in mineral sassolite, but dissolves in water. H$_4$CN$_2$O, urea, has mp. of only 133 °C and thiourea has overall better properties. PNCl$_2$ is phosphazene with 6-membered ring with alternating P and N, but mp. of 112 °C is too low. PNCIF and PBrNF are similar and, though they are stable at RT, the mp. is likely low as in other phosphorus halides [29]. CCl$_3$, cyanuric chloride, consists of 6-membered ring with alternating C and N, but mp. of 112 °C. Thus, from this set, we found only two clearly promising materials to be used as a substrate: As$_2$O$_3$, P$_2$O$_5$. Possibly interesting candidates are magnesium perchlorate and boric acid.

Finally, it is worth highlighting few specific data points in Fig. 1(b). The material with dielectric constant over 40 is H$_2$Pt((OH)$_6$) platinitic acid. In crystalline form, it is experimentally stable to about 150 °C, after which it starts to form PtO$_2$ [30]. The calculated $E_{\text{hull}} = 0.069$ eV/atom also suggests poor stability. There are also three high melting point materials, shown by red markers, in Fig. 1(b): PtCl$_2$, PdCl$_2$, and NbI$_5$. The Pt and Pd chlorides in β-phase consist of octahedral cage structure with six formula units (hexamer). PdCl$_2$ and PtCl$_2$ are reported to have high mp. of 581 and 679 °C, respectively, but those values correspond to the polymeric α-phase. There is a phase transition from β- to α-phase at around 500 °C[31], which is still high. The calculated band gaps are less than 2 eV and dielectric constant 3–4. NbI$_5$ is a molecular dimer with mp. 543 °C, gap 1.0 eV, and $\varepsilon^0_{\text{poly}} = 8.8$.

From this database search, we have ended up with 8 materials in 6 cluster prototypes that showed high melting points and reasonably high band gap and dielectric constant: adamantane (Sb$_4$O$_6$, As$_4$O$_6$), uzonite (As$_4$S$_5$), realgar (As$_4$S$_4$) terminated adamantane (denoted T-adamantane, P$_4$O$_{10}$), metal halide hexamer (MH-hexamer, Pt$_6$Cl$_{12}$, Pd$_6$Cl$_{12}$), and metal halide dimer (MH-dimer, Nb$_2$I$_{10}$). The prototype cluster structures are visualized in Fig. 1.

We now revisit the materials for which calculated dielectric constant was not available in MP. We represented all cluster structures as connected graphs and then searched for graphs that are isomorphic to the prototype systems among those where dielectric constant was not available. We stress, that this approach only considers the connectivity/bonding network between atoms, but ignores the atom types and thus, for example, P$_4$O$_{10}$ and P$_4$S$_4$O$_6$ are isomorphic despite having only a fraction of the oxygens replaced by sulfur. This search yielded in total 27 structures, 3 adamantanes, 1 uzonite-like, 2 realgar-like, 3 T-adamantanes, 0 MH-hexamer, 18 MH-dimer. These are listed in Table S2. We again pruned the list by removing low mp. and metastable systems, and those with zero or vanishingly small band gap. It is worth noting that four of the metal halide dimers with zero band gap also exhibited nonzero magnetic moment. We are left with 12 additional materials: uzonite-like As$_4$Se$_4$ with mp. of 265 °C; T-adamantane P$_4$S$_{10}$, Ge$_4$S$_6$Br$_4$, Ge$_4$S$_6$I$_4$ all have mp close to 300 °C; MH-dimers Nb$_2$Br$_{10}$ and Ta$_2$Br$_{10}$ have mp. 250–300 °C, Nb$_2$Cl$_{10}$ has mp. close to 200 °C, and Ta$_2$I$_{10}$ has mp. of 382 °C.
2.2 Cluster properties

From the screening study presented thus far, we are left with 16 materials in the 6 prototypes. Since Materials Project data is calculated using PBE functional that poorly describes van der Waals interactions, we recalculated these systems, both crystalline and isolated clusters, using vdw-DF functional. Selected properties are collected in Table 1 such as binding energies, band gaps and dielectric constants, and additional properties are listed in Table S3. The experimental melting point is also included for convenience in Table 1.

The binding energies per cluster are usually few eVs, which may appear quite large, but the sizes of these clusters and the areas between them are also significant. We estimate binding energy per area by mapping the volume per molecule in a crystal to a sphere and taking its area. These values fall within 6–40 meV/Å, which is comparable to the 2D material binding energies, where majority of compounds fall within 13–21 meV/Å [32, 33]. Thus, it appears safe to label these systems as vdw-bonded 0D materials. In Table 1 we also listed the gaps calculated using vdw-DF for crystals and for isolated clusters. Comparing to the MP gaps listed in Tables S1 and S2, shows that, as van der Waals interaction pulls the clusters closer together, the band gap decreases: 0.4–0.5 eV decrement is seen for many materials, except for As$_2$O$_3$ and P$_2$O$_5$ which remain largely unaffected. The lowering of the band gap is in turn reflected in slight increase of the dielectric constants, see also the plot of band gap vs. dielectric constant shown in Fig. 3(a). Conversely, the HOMO-LUMO gaps of the isolated clusters are higher than the crystal gaps by about 0.5–1 eV.

For nanoelectronics applications, it is important to know the alignment of the valence band maxima and conduction band minima of the 0D materials with respect to the band extrema of the 2D materials. Here, we evaluated this from the HOMO and LUMO levels of isolated clusters and the results are shown in Fig. 3(b). Adamantanes, uzonite, realgars, and some of T-adamantanes have all suitable band edge positions compared to common 2D materials. Metal halide hexamer and dimer band edges are deep and as a result the LUMO level of 0D cluster are below the conduction band minima of most 2D materials. 0D materials have several natural cleaving planes, that lead to 2D layers of clusters with different orientations and different lattices, depending on the symmetry of the clusters and of the 3D lattice. It is not a priori clear what will be the preferred orientation and ordering of the clusters when sputtered on top of a particular 2D material and how to control the growth mode [12]. Investigating this by first-principles calculations is highly demanding.

![Figure 2: Atomic structures of the cluster prototypes.](image)
Table 1: Selected properties of promising 0D materials calculated using vdW-DF functional: cluster formula, binding energy per area (meV/Å), band gap from crystal (eV), HOMO-LUMO gap from cluster (eV), and static and high-frequency dielectric constants. The experimental melting points (mp., in °C) are also included for convenience.

| formula   | binding energy | mp.  | Crystal gap | Cluster gap | \( \varepsilon_\infty^{\text{poly}} \) | \( \varepsilon_0^{\text{poly}} \) |
|-----------|----------------|------|-------------|-------------|-----------------|-----------------|
| Sb\(_2\)O\(_6\) | -30.37 | 656.0 | 2.92 | 4.09 | 3.95 | 10.92 |
| As\(_4\)S\(_5\) | -18.66 | 656.0 | 1.42 | 2.64 | 6.31 | 8.10 |
| As\(_4\)S\(_4\) | -17.29 | 320.0 | 1.38 | 2.80 | 6.00 | 7.91 |
| As\(_4\)O\(_6\) | -18.30 | 312.2 | 4.04 | 4.49 | 2.59 | 4.92 |
| P\(_4\)O\(_10\) | -18.64 | 340.0 | 5.47 | 6.01 | 1.37 | 2.41 |
| Pt\(_6\)Cl\(_{12}\) | -6.15  | 581.0 | 1.48 | 2.01 | 3.99 | 4.19 |
| Pd\(_6\)Cl\(_{12}\) | -6.50  | 679.0 | 1.09 | 1.64 | 6.25 | 6.80 |
| Nb\(_2\)I\(_{10}\) | -8.04  | 543.0 | 0.61 | 1.08 | 9.98 | 15.01 |
| As\(_4\)Se\(_4\) | -39.87 | 265.0 | 0.85 | 2.17 | 10.69 | 12.61 |
| P\(_4\)S\(_10\) | -12.33 | 288.0 | 2.17 | 2.97 | 3.98 | 4.60 |
| Ge\(_2\)S\(_6\)Br\(_4\) | -11.46 | 305.0 | 2.14 | 2.79 | 3.40 | 4.22 |
| Ge\(_2\)S\(_6\)I\(_4\) | -11.02 | 310.0 | 2.06 | 2.59 | 3.85 | 4.75 |
| Nb\(_2\)Br\(_{10}\) | -26.47 | 254.0 | 1.37 | 1.70 | 4.72 | 7.13 |
| Ta\(_2\)Br\(_{10}\) | -18.94 | 265.0 | 1.86 | 2.19 | 3.85 | 5.79 |
| Nb\(_2\)Cl\(_{12}\) | -17.27 | 204.7 | 2.07 | 2.33 | 3.12 | 4.99 |
| Ta\(_2\)I\(_{10}\) | -30.31 | 382.0 | 0.94 | 1.41 | 7.25 | 10.54 |

To shed light on the interaction of the clusters with 2D materials, we first studied the interaction of isolated 0D clusters placed on a monolayer MoS\(_2\). The density of states for all 16 cases are collected in Fig. S4 and shows that the MoS\(_2\) states are largely unaffected by the 0D cluster, evidencing that the interaction is weak. Moreover, in Fig. S4 we also indicate the binding energies. For the interaction area we have again transformed the volume per cluster to a sphere (as mentioned above) and taken its great circle. The values fall within 10–20 meV/Å, again similar to those reported above and as reported for many 2D materials, providing evidence to the vdW-type binding with the 2D material.

Next, as an example, we constructed one heterostructure with the surface of WSe\(_2\) fully covered by As\(_2\)O\(_3\). Due to the similarity of As\(_2\)O\(_3\) and Sb\(_2\)O\(_3\), the structure of 0D clusters on the surface is also likely similar, and thus we can adopt for As\(_2\)O\(_3\) the experimentally determined structure of Sb\(_2\)O\(_3\). For the 2D material we chose WSe\(_2\) due to suitable lattice constant, which allowed us to construct heterostructure model with minimal strain. As\(_2\)O\(_3\) has higher band gap than Sb\(_2\)O\(_3\) but smaller dielectric constant and thus useful as a low-\(\kappa\) dielectric or, e.g., as a substrate for studying single-photon emitters in WSe\(_2\) [34, 35] without interference from the substrate defects. The optimized atomic structure is shown in Fig. 3(c).

The atomic structures of both the WSe\(_2\) and As\(_2\)O\(_3\) layers are very weakly perturbed by the neighboring layer, indicating again van der Waals type interaction. Similarity of the effective band structure of the heterostructure and the band structure of pristine WSe\(_2\) in Fig. 3(d) demonstrates that the band structures of As\(_2\)O\(_3\) and WSe\(_2\) are effectively uncoupled. The As\(_2\)O\(_3\) bands with very small dispersion are seen at about 2 eV below valence band maximum and about 1 eV above conduction band minimum of WSe\(_2\). Thus, charge transfer to/from the As\(_2\)O\(_3\) should not occur and we expect the electronic and optical properties of WSe\(_2\) layers to remain largely intact.

3 Conclusion

In conclusion, we have extracted a list of promising 0D materials to be used with 2D materials in nanoelectronics applications, exhibiting fairly high band gaps, dielectric constants, and melting points. This was achieved by screening Materials Project database, combining it with experimental melting points, and using graph-theoretical methods to find other similar structures. We used first-principles calculations to predict additional material properties and studied the interaction of the 0D clusters with a prototypical 2D materials MoS\(_2\). All these materials were confirmed to have binding energies typical for vdW-bonded systems and to weakly perturb the electronic structure of the 2D material.

Owing to the vdW gaps between clusters, their conductivity is expected to be low and thus they should...
be fairly good insulators even though their band gaps in the crystalline form are not very high. Consequently, “metallic” 0D materials do not appear particularly promising as electrode materials. In addition to their use as a gate dielectric or substrate, these 0D materials could be used as spacer layers in 2D material superlattices [36]. Intercalation between 2D layers can also stabilize crystalline order for clusters that have too low melting point in 3D lattice. For instance, superlattices of 2D materials and CTAB (and other related) molecules was demonstrated in [37]. Also, AlCl₃ and CuCl₂ clusters and various dimerized and trimerized forms of them have successfully been intercalated between graphene sheets [38]. Although materials consisting of more than one type of clusters were ignored in this Letter for reasons of simplicity, a vast variety of such 0D molecular compounds could exist. As an example, 2D crystal made of SbI₃ and S₈ molecular units was reported in Ref. [39]. We hope that the our study motivates further experimental and computational work on these materials. Based on the cluster prototypes identified here, other 0D materials could be identified or purposefully

Figure 3: Properties from vdW-DF calculations. (a) Band gap vs. static dielectric constant. Marker color indicates the melting point or black if unknown. (b) HOMO and LUMO levels of 0D clusters aligned via vacuum level. The materials are grouped and colored according to the cluster prototype. (c) Top and side vies of atomic structure of As₂O₃ on WSe₂. Dashed rhombus denotes the As₂O₃ surface unit cell. (d) Effective band structure of the heterostructure model (underlying gray features) compared to the band structure of pristine WSe₂ (overlaid lines). The local DOS of As₂O₃ and WSe₂ layers are also shown.
designed, either by substitution or by addition of functional groups. These can extend the range of properties or provide even new functionalities, such as charge doping or magnetism.

4 Methods

The material information were extracted from Materials Project we used the REST API [40]. The structures were then fed into the dimensionality analysis tools as implemented in ASE [41]. The graph-theoretical part was done using NetWorkX package [42]. All density-functional theory calculations were carried out using VASP software [43, 44], together with projector augmented plane wave method. We adopted Hamada’s rev-VDW-DF2 functional [45, 46, 47, 48], which was found to yield good structural properties and interlayer binding energies for 2D materials [33]. Most other input parameters were taken from the Materials Project [17, 40], such as the k-point meshes and the plane wave cutoff of 520 eV. Isolated molecules on MoS$_2$ were modeled using 4×4 supercell of MoS$_2$ and a 3×3 k-point mesh. For the heterostructure of As$_2$O$_3$ and WSe$_2$, we take the (111) plane of As$_2$O$_3$. This has lattice constant of 7.715 Å, in which case a 3×3 supercell (23.144 Å) matches closely with a 7×7 supercell of WSe$_2$ (7·3.297 = 23.079 Å). In the heterostructure model, we keep the lattice constant of WSe$_2$ fixed and compressively strain As$_2$O$_3$ layer by 0.28%. We used 2×2 k-point mesh during relaxation and 4×4 k-point mesh in calculating density of states. Effective band structure was calculated using BandUP code [49].

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

We thank CSC–IT Center for Science Ltd. for generous grants of computer time.

Conflict of Interest

The authors declare no conflict of interest.

References

[1] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, A. Kis, Nature Nanotechnology 2011, 6, 3 147.
[2] C. Liu, H. Chen, X. Hou, H. Zhang, J. Han, Y.-G. Jiang, X. Zeng, D. W. Zhang, P. Zhou, Nature Nanotechnology 2019, 14, 7 662.
[3] G. Migliato Marega, Y. Zhao, A. Avsar, Z. Wang, M. Tripathi, A. Radenovic, A. Kis, Nature 2020, 587, 7832 72.
[4] S. Bertolazzi, D. Krasnozhon, A. Kis, ACS Nano 2013, 7, 4 3246.
[5] C. Liu, X. Yan, X. Song, S. Ding, D. W. Zhang, P. Zhou, Nature Nanotechnology 2018, 13, 5 404.
[6] V. K. Sangwan, D. Jariwala, I. S. Kim, K.-S. Chen, T. J. Marks, L. J. Lauhon, M. C. Hersam, Nature Nanotechnology 2015, 10, 5 403.
[7] R. Ge, X. Wu, M. Kim, J. Shi, S. Sonde, L. Tao, Y. Zhang, J. C. Lee, D. Akinwande, Nano Letters 2018, 18, 1 434, pMID: 29236504.
[8] X. Zhang, J. Grajal, J. L. Vazquez-Roy, U. Radhakrishna, X. Wang, W. Chern, L. Zhou, Y. Lin, P.-C. Shen, X. Ji, X. Ling, A. Zubair, Y. Zhang, H. Wang, M. Dubey, J. Kong, M. Dresselhaus, T. Palacios, Nature 2019, 566, 7744 368.
[9] C. Liu, H. Chen, S. Wang, Q. Liu, Y.-G. Jiang, D. W. Zhang, M. Liu, P. Zhou, Nature Nanotechnology 2020, 15, 7 545.
[10] W. Han, P. Huang, L. Li, F. Wang, P. Luo, K. Liu, X. Zhou, H. Li, X. Zhang, Y. Cui, T. Zhai, *Nature Communications* **2019**, *10*, 1 4728.

[11] K. Liu, B. Jin, W. Han, X. Chen, P. Gong, L. Huang, Y. Zhao, L. Li, S. Yang, X. Hu, J. Duan, L. Liu, F. Wang, F. Zhuge, T. Zhai, *Nature Electronics* **2021**, *4*, 12 906.

[12] K. Liu, L. Liu, T. Zhai, *The Journal of Physical Chemistry Letters* **2022**, *13*, 9 2173, pMID: 35230116.

[13] S. Lebègue, T. Björkman, M. Klintenberg, R. M. Nieminen, O. Eriksson, *Phys. Rev. X* **2013**, *3*, 031002.

[14] G. Cheon, K.-A. N. Duerloo, A. D. Sendek, C. Porter, Y. Chen, E. J. Reed, *Nano Letters* **2017**, *17*, 3 1915, pMID: 28191965.

[15] N. Mounet, M. Gibertini, P. Schwaller, D. Campi, A. Merkys, A. Marrazzo, T. Sohier, I. E. Castelli, A. Cepellotti, G. Pizzi, N. Marzari, *Nature Nanotechnology* **2018**, *13*, 3 246.

[16] R. Friedrich, M. Ghorbani-Asl, S. Curtarolo, A. V. Krasheninnikov, *Nano Letters* **2022**, *22*, 3 989, pMID: 35051335.

[17] A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, K. a. Persson, *APL Materials* **2013**, *1*, 1 011002.

[18] P. Gorai, E. S. Toberer, V. Stevanović, *J. Mater. Chem. A* **2016**, *4*, 11110.

[19] P. M. Larsen, M. Pandey, M. Strange, K. W. Jacobsen, *Phys. Rev. Materials* **2019**, *3*, 034003.

[20] W. Storzer, D. Schomburg, G.-V. Röschenthaler, R. Schmutzler, *Chemische Berichte* **1983**, *116*, 1 367.

[21] J. Rosdahl, M. Gorlov, A. Fischer, L. Kloo, *Zeitschrift für anorganische und allgemeine Chemie* **2004**, *630*, 5 760.

[22] A. Benrath, B. Schifers, *Zeitschrift für anorganische und allgemeine Chemie* **1938**, *240*, 1 67.

[23] H. J. Whitfield, *J. Chem. Soc., Dalton Trans.* **1973**, 1740–1742.

[24] H.-P. Komsa, A. V. Krasheninnikov, *Phys. Rev. B* **2012**, *86* 241201.

[25] Y. Lin, X. Ling, L. Yu, S. Huang, A. L. Hsu, Y.-H. Lee, J. Kong, M. S. Dresselhaus, T. Palacios, *Nano Letters* **2014**, *14*, 10 5569, pMID: 25216267.

[26] A. Chernikov, T. C. Berkelbach, H. M. Hill, A. Rigosi, Y. Li, O. B. Aslan, D. R. Reichman, M. S. Hybertsen, T. F. Heinz, *Phys. Rev. Lett.* **2014**, *113* 076802.

[27] M. M. Ugeda, A. J. Bradley, S.-F. Shi, F. H. da Jornada, Y. Zhang, D. Y. Qiu, W. Ruan, S.-K. Mo, Z. Hussain, Z.-X. Shen, F. Wang, S. G. Louie, M. F. Crommie, *Nature Materials* **2014**, *13*, 12 1091.

[28] K. Waizumi, H. Masuda, H. Ohtaki, *Inorganica Chimica Acta* **1992**, *192*, 2 173.

[29] P. Clare, T. J. King, D. B. Sowerby, *J. Chem. Soc., Dalton Trans.* **1974**, 2071–2074.

[30] A. B. Venediktov, S. V. Korenev, D. B. Vasil’chenko, A. V. Zadesenets, E. Y. Filatov, S. N. Mamonov, L. V. Ivanova, N. G. Prudnikova, E. Y. Semitut, *Russian Journal of Applied Chemistry* **2012**, *85*, 7 995.

[31] B. Krebs, C. Brendel, H. Schäfer, *Zeitschrift für anorganische und allgemeine Chemie* **1988**, *561*, 1 119.

[32] T. Björkman, A. Gulans, A. V. Krasheninnikov, R. M. Nieminen, *Phys. Rev. Lett.* **2012**, *108* 235502.
[33] T. Björkman, *The Journal of Chemical Physics* **2014**, *141*, 7 074708.

[34] C. Chakraborty, L. Kinnischtzke, K. M. Goodfellow, R. Beams, A. N. Vamivakas, *Nature Nanotechnology* **2015**, *10*, 6 507.

[35] M. Toth, I. Aharonovich, *Annual Review of Physical Chemistry* **2019**, *70*, 1 123, pMID: 30735459.

[36] P. Kumar, J. Lynch, B. Song, H. Ling, F. Barrera, K. Kisslinger, H. Zhang, S. B. Anantharaman, J. Digani, H. Zhu, T. H. Choudhury, C. McAleese, X. Wang, B. R. Conran, O. Whear, M. J. Motlala, M. Snure, C. Muratore, J. M. Redwing, N. R. Glavin, E. A. Stach, A. R. Davoyan, D. Jariwala, *Nature Nanotechnology* **2022**, *17*, 2 182.

[37] C. Wang, Q. He, U. Halim, Y. Liu, E. Zhu, Z. Lin, H. Xiao, X. Duan, Z. Feng, R. Cheng, N. O. Weiss, G. Ye, Y.-C. Huang, H. Wu, H.-C. Cheng, I. Shakir, L. Liao, X. Chen, W. A. Goddard III, Y. Huang, X. Duan, *Nature* **2018**, *555*, 231.

[38] Y.-C. Lin, A. Motoyama, S. Kretschmer, S. Ghaderzadeh, M. Ghorbani-Asl, Y. Araki, A. V. Krasheninnikov, H. Ago, K. Suenaga, *Advanced Materials* **2021**, *33*, 52 2105898.

[39] X. Feng, Z. Sun, K. Pei, W. Han, F. Wang, P. Luo, J. Su, N. Zuo, G. Liu, H. Li, T. Zhai, *Advanced Materials* **2020**, *32*, 32 2003146.

[40] S. P. Ong, S. Cholia, A. Jain, M. Brafman, D. Gunter, G. Ceder, K. A. Persson, *Computational Materials Science* **2015**, *97*, 209.

[41] A. H. Larsen, J. J. Mortensen, J. Blomqvist, I. E. Castelli, R. Christensen, M. Dulak, J. Friis, M. N. Groves, B. Hammer, C. Hargus, E. D. Hermes, P. C. Jennings, P. B. Jensen, J. Kermode, J. R. Kitchin, E. L. Kolsbjerg, J. Kubal, K. Kaasbjerg, S. Lysgaard, J. B. Maronsson, T. Maxson, T. Olsen, L. Pastewka, A. Peterson, C. Rostgaard, J. Schiøtz, O. Schütt, M. Strange, K. S. Thygesen, T. Vegge, L. Vilhelmsen, M. Walter, Z. Zeng, K. W. Jacobsen, *Journal of Physics: Condensed Matter* **2017**, *29*, 27 273002.

[42] A. Hagberg, P. Swart, D. S Chult, Exploring network structure, dynamics, and function using networkx, Technical report, Los Alamos National Lab.(LANL), Los Alamos, NM (United States), 2008.

[43] G. Kresse, J. Furthmüller, *Phys. Rev. B* **1996**, *54* 11169.

[44] G. Kresse, D. Joubert, *Phys. Rev. B* **1999**, *59* 1758.

[45] I. Hamada, *Phys. Rev. B* **2014**, *89* 121103.

[46] M. Dion, H. Rydberg, E. Schröder, D. C. Langreth, B. I. Lundqvist, *Phys. Rev. Lett.* **2004**, *92* 246401.

[47] G. Román-Pérez, J. M. Soler, *Phys. Rev. Lett.* **2009**, *103* 096102.

[48] J. c. v. Klimeš, D. R. Bowler, A. Michaelides, *Phys. Rev. B* **2011**, *83* 195131.

[49] P. V. C. Medeiros, S. Stafström, J. Björk, *Phys. Rev. B* **2014**, *89* 041407.
I. TABLES

| Name                        | Formula          | Cluster                          | MP-ID     | $E_{\text{hull}}$ (in eV) | $E_g$ (in eV) | $\varepsilon_0$ | mp.            | bp.            | source     |
|-----------------------------|------------------|----------------------------------|-----------|--------------------------|--------------|---------------|----------------|----------------|------------|
| aluminum borohydride        | Al(BH4)3         | Al(BH4)3                         | mp-569787| 0.0                      | 6.24         | 3.40          | -64.5          | 44.5           | Wikipedia  |
| aluminium iodide            | AlI3             | Al2I6                             | mp-30930  | 0.0                      | 3.27         | 3.73          | 188.3          | 382.0          | Wikipedia  |
| arsenic trioxide (cubic)    | As2O3            | As4O6                             | mp-2184   | 0.009                    | 4.03         | 3.83          | 312.2          | 465.0          | Wikipedia  |
| uzonite                     | As4S5            | As4S5                             | mp-502    | 0.003                    | 2.01         | 5.45          |                |                |            |
| arsenic trichloride         | AsCl3            | AsCl3                             | mp-23280  | 0.0                      | 4.10         | 3.33          | -16.2          | 130.2          | Wikipedia  |
| arsenic pentafluoride       | AsF5             | AsF5                              | mp-8723   | 0.0                      | 4.63         | 2.35          | -79.8          | -52.8          | Wikipedia  |
| realgar                     | AsS              | AsS                               | mp-542846 | 0.004                    | 2.05         | 5.24          | 8.5            | 60.4           | Wikipedia  |
| gold chloride               | AuCl3            | Au2Cl6                            | mp-27647  | 0.0                      | 1.39         | 3.93          | 254.0          |                | Wikipedia  |
| boric acid                  | B(HO)3           | B(HO)3                            | mp-759069 | 0.003                    | 6.09         | 2.81          | 1.70           | 300.0          | Wikipedia  |
| boron tribromide            | BBr              | B9Br9                             | mp-685043 | 0.009                    | 1.43         | 3.71          |                |                |            |
| boron trichloride           | BC13             | BC13                              | mp-23184  | 0.0                      | 4.75         | 2.20          | -107.3         | 12.6           | Wikipedia  |
| boron trifluoride           | BF3              | BF3                               | mp-558149 | 0.0                      | 8.16         | 2.19          | -126.8         | -100.3         | Wikipedia  |
| ammonia borane              | BNH6             | BNH6                              | mp-35082  | 0.001                    | 6.07         | 5.19          | 104.0          |                | Wikipedia  |
| bromine pentafluoride       | BrF5             | BrF5                              | mp-27987  | 0.0                      | 3.46         | 3.16          | -61.3          | 40.2           | Wikipedia  |
| bromine trifluoride         | BrF3             | BrF3                              | mp-23225  | 0.0                      | 3.87         | 2.37          | -46.3          | 91.3           | Wikipedia  |
| cyanuric chloride           | CNCl             | (NCCl)3                           | mp-571324 | 0.0                      | 3.79         | 2.78          | 144.0          | 192.0          | Wikipedia  |
| dichlorodifluoromethane     | C2ClF2           | C2ClF2                            | mp-22966  | 0.015                    | 5.74         | 2.43          | -157.7         | -29.8          | Wikipedia  |
| dichlorotrifluoromethane    | CC1F3            | CC1F3                             | mp-23071  | 0.012                    | 4.90         | 3.15          | -110.5         | 23.8           | Wikipedia  |
| tetrafluoromethane          | CF4              | CF4                               | mp-1167   | 0.0                      | 9.07         | 1.93          | -183.6         | -127.8         | Wikipedia  |
| carbon disulfide            | CNCl             | (NCCl)3                           | mp-571324 | 0.0                      | 3.79         | 2.78          | 144.0          | 192.0          | Wikipedia  |
| chlorine trifluoride        | CIF3             | CIF3                              | mp-556767 | 0.005                    | 2.63         | 3.52          | -76.3          | 11.8           | Wikipedia  |
| CoBr2.4H2O                  | CoH8(BrO2)2      | CoH8(BrO2)2                       | mp-23965  | 0.053                    | 2.20         | 5.03          |                |                |            |
| * chromium hexafluoride     | CrF6             | CrF6                              | mp-1539213| 0.0                      | 2.09         | 3.21          |                |                |            |
| Gallium carbide             | GaBr3            | Ga2Br6                            | mp-30953  | 0.0                      | 3.36         | 3.37          | 121.5          | 278.8          | Wikipedia  |
| gallium trichloride         | GaCl3            | Ga2Cl6                            | mp-30952  | 0.0                      | 4.28         | 3.36          | 77.9           | 201.0          | Wikipedia  |
| germanium tetrachloride     | GeCl4            | GeCl4                             | mp-30086  | 0.0                      | 4.27         | 2.56          | -49.5          | 86.5           | Wikipedia  |
| germanium tetrafluoride     | GeF4             | GeF4                              | mp-9816   | 0.0                      | 5.68         | 2.69          | -15.0          | -36.5          | Wikipedia  |
| germeyl chloride            | GeH3Cl           | GeH3Cl                            | mp-28369  | 0.0                      | 4.76         | 3.78          | 0.0            |                |            |
| Chemical Name         | Formula     | mp (°C) | delta (°C) | delta (°C) | delta (°C) | delta (°C) | delta (°C) | delta (°C) | Reference   |
|-----------------------|-------------|---------|------------|------------|------------|------------|------------|------------|-------------|
| Hydrogen peroxide     | H₂O₂        | 150.2   | 150.2      | 150.2      | 150.2      | 150.2      | 150.2      | 150.2      | [1] Wikipedia |
| Sulfuric acid         | H₂SO₄       | 390.0   | 390.0      | 390.0      | 390.0      | 390.0      | 390.0      | 390.0      | [2] Wikipedia |
| Selenous acid         | H₂SeO₃      | 182.0   | 182.0      | 182.0      | 182.0      | 182.0      | 182.0      | 182.0      | [3] Wikipedia |
| Selenic acid          | H₂SeO₄      | 304.0   | 304.0      | 304.0      | 304.0      | 304.0      | 304.0      | 304.0      | [4] Wikipedia |
| Ammonia               | H₃N         | 130.0   | 130.0      | 130.0      | 130.0      | 130.0      | 130.0      | 130.0      | [5] Wikipedia |
| Methane               | CH₄         | 161.5   | 161.5      | 161.5      | 161.5      | 161.5      | 161.5      | 161.5      | [6] Wikipedia |
| Urea                  | CH₄N₂O      | 251.0   | 251.0      | 251.0      | 251.0      | 251.0      | 251.0      | 251.0      | [7] Wikipedia |
| Thiourea              | CH₄N₂S      | 304.0   | 304.0      | 304.0      | 304.0      | 304.0      | 304.0      | 304.0      | [8] Wikipedia |
| Thioformaldehyde      | CH₄S₂O      | 679.0   | 679.0      | 679.0      | 679.0      | 679.0      | 679.0      | 679.0      | [9] Wikipedia |
| Iodic acid            | HIO₃        | 405.0   | 405.0      | 405.0      | 405.0      | 405.0      | 405.0      | 405.0      | [10] Wikipedia |
| Mercury bromide       | HgBr₂       | 405.0   | 405.0      | 405.0      | 405.0      | 405.0      | 405.0      | 405.0      | [11] Wikipedia |
| Mercury chloride      | HgCl₂       | 304.0   | 304.0      | 304.0      | 304.0      | 304.0      | 304.0      | 304.0      | [12] Wikipedia |
| Iodine trifluoride    | I₂Cl₆       | 63.0    | 63.0       | 63.0       | 63.0       | 63.0       | 63.0       | 63.0       | [13] Wikipedia |
| Iodine heptafluoride  | IF₇         | 4.8     | 4.8        | 4.8        | 4.8        | 4.8        | 4.8        | 4.8        | [14] Wikipedia |
| Magnesium perchlorate | Mg(ClO₄)₂(H₂O)₄ | 251.0    | 251.0      | 251.0      | 251.0      | 251.0      | 251.0      | 251.0      | [15] Wikipedia |
| Molybdenum hexafluoride| MoF₆       | 34.0    | 34.0       | 34.0       | 34.0       | 34.0       | 34.0       | 34.0       | [16] Wikipedia |
| Chlorine nitrate      | Cl₂O₄       | 180.0   | 180.0      | 180.0      | 180.0      | 180.0      | 180.0      | 180.0      | [17] Wikipedia |
| Nitric oxide          | N₂O₄       | 250.0   | 250.0      | 250.0      | 250.0      | 250.0      | 250.0      | 250.0      | [18] Wikipedia |
| Nitrogen tetroxide    | N₂O₅       | 129.7   | 129.7      | 129.7      | 129.7      | 129.7      | 129.7      | 129.7      | [19] Wikipedia |
| Phosphorus pentoxide  | P₂O₅        | 360.0   | 360.0      | 360.0      | 360.0      | 360.0      | 360.0      | 360.0      | [20] Wikipedia |
| Phosphorus trioxide   | P₃O₅       | 295.0   | 295.0      | 295.0      | 295.0      | 295.0      | 295.0      | 295.0      | [21] Wikipedia |
| Phosphorus pentafluoride| PF₅        | 84.6    | 84.6       | 84.6       | 84.6       | 84.6       | 84.6       | 84.6       | [22] Wikipedia |
| Phosphorus trifluoride| PF₃        | 41.5    | 41.5       | 41.5       | 41.5       | 41.5       | 41.5       | 41.5       | [23] Wikipedia |
| Phosphorus pentafluoride| PF₅        | 84.6    | 84.6       | 84.6       | 84.6       | 84.6       | 84.6       | 84.6       | [24] Wikipedia |
| Phosphorus hexafluoride| PF₆        | 189.5   | 189.5      | 189.5      | 189.5      | 189.5      | 189.5      | 189.5      | [25] Wikipedia |
| Phosphorus pentafluoride| PF₅        | 84.6    | 84.6       | 84.6       | 84.6       | 84.6       | 84.6       | 84.6       | [26] Wikipedia |
| Phosphorus octafluoride| PF₈        | 584.0   | 584.0      | 584.0      | 584.0      | 584.0      | 584.0      | 584.0      | [27] Wikipedia |
| Phosphorus hexafluoride| PF₆        | 189.5   | 189.5      | 189.5      | 189.5      | 189.5      | 189.5      | 189.5      | [28] Wikipedia |
| Phosphorus heptafluoride| PF₇        | 34.0    | 34.0       | 34.0       | 34.0       | 34.0       | 34.0       | 34.0       | [29] Wikipedia |
| Palladium chloride    | PdCl₂       | 679.0   | 679.0      | 679.0      | 679.0      | 679.0      | 679.0      | 679.0      | [30] Wikipedia |
| Name                        | Formula | Cluster | MP-ID     | $E_{\text{null}}$ | $E_g$ | $\varepsilon_0$ | mp. | bp. | source |
|-----------------------------|---------|---------|-----------|-------------------|-------|-----------------|-----|-----|--------|
| platinum chloride          | PtCl2   | Pt6Cl12 | mp-23290  | 0.0               | 1.83  | 3.29            | 581.0 |     | Wikipedia |
| perrenic acid               | Re2H4O9 | Re2O7(H2)2 | mp-625238 | 0.026             | 2.64  | 11.38           | 115.0 |     | [30]   |
| ruthenium tetroxide         | Ru2O4   | RuO3    | mp-554791 | 0.0               | 2.43  | 2.77            | 25.4  | 40.0 | Wikipedia |
| sulfur (alpha)              | S       | S8      | mp-77     | 0.001             | 2.71  | 2.95            | 115.2  | 444.6 | Wikipedia |
| sulfur (alpha)              | S       | S12     | mp-558014 | 0.014             | 2.48  | 3.09            | -     |     |        |
| sulfur (alpha)              | S       | S14     | mp-561513 | 0.019             | 2.43  | 3.44            | -     |     |        |
| sulfuryl chloride           | S(ClO)2 | S2O2Cl2 | mp-28405  | 0.0               | 3.79  | 3.46            | -54.1  | 69.4 | Wikipedia |
| sulfur trioxide             | S       | S3O9    | mp-2414   | 0.0               | 5.14  | 2.78            | 16.9  | 45.0 | Wikipedia |
| antimony trioxide           | Sb2O3   | Sb4O6   | mp-1999   | 0.008             | 3.41  | 8.42            | 656.0  | 1425.0 | Wikipedia |
| antimony tribromide         | SbBr3   | Sb3Br   | mp-27399  | 0.0               | 3.45  | 4.00            | 96.6  | 288.0 | Wikipedia |
| antimony trichloride        | SbCl3   | SbCl3   | mp-22872  | 0.0               | 3.75  | 7.67            | 73.4  | 223.5 | Wikipedia |
| selenium (beta)             | Se      | Se8     | mp-542605 | 0.006             | 1.40  | 5.33            | 221.0  | 685.0 | Wikipedia |
| diseleneniodibromid         | SeBr    | Br2Se2  | mp-570589 | 0.006             | 1.55  | 6.31            | -49.0  | 225.0 | [35]   |
| selenium tetrafluoride      | SeF4    | F2OSe   | mp-29172  | 0.0               | 4.14  | 6.68            | -13.2  | 101.0 | Wikipedia |
| seleninyl difluoride        | SeOF2   | Cl2SiO4 | mp-28959  | 0.026             | 5.68  | 2.94            | -      |       |        |
| octahydratosilsesquioxane   | Si2H2O3 | Si2HO3 | mp-24431  | 0.026             | 3.37  | 3.23            | -      |       |        |
| disiloxane                  | Si2H6O  | Si2H6O | mp-27949  | 0.050             | 5.26  | 2.86            | -15.2  | -15.2 | Wikipedia |
| disilyl selenide            | Si2H6Se | Si2H6Se| mp-29310  | 0.000             | 3.75  | 6.32            | -68.0  | 85.0  | [40]   |
| silicon tetrabromide        | SiBr4   | SiBr4   | mp-570285 | 0.0               | 4.11  | 2.61            | 5.0    | 153.0 | Wikipedia |
| cyclic chlorosiloxane       | SiC12O  | SiC12O  | mp-23079  | 0.015             | 5.57  | 2.81            | 77.0   |       | [41]   |
| cyclic chlorosiloxane       | SiC12O  | SiC12O3 | mp-23563  | 0.027             | 5.57  | 2.64            | 43.5   |       | [41]   |
| silicon tetrafluoride       | SiF4    | SiF4    | mp-1818   | 0.0               | 7.94  | 2.16            | -95.0  | -90.0 | [42]   |
| silyl fluoride              | SiH3F   | SiH3F   | mp-28289  | 0.024             | 6.01  | 2.62            | -98.6  |       | [42]   |
| iodosilane                 | SiH3I   | SiH3I   | mp-28538  | 0.0               | 4.21  | 3.70            | -57.0  | 45.4  | [43]   |
| silane                      | SiH4    | SiH4    | mp-23739  | 0.005             | 6.59  | 2.47            | -185.0 | -119.9| Wikipedia |
| silicon tetrafluoride       | SiF4    | SiF4    | mp-643277 | 0.0               | 6.70  | 3.21            | 166.0  |       | [44]   |
| tin iodide                  | SnI4    | SnI4    | mp-571436 | 0.019             | 1.78  | 3.40            | 143.0  | 348.5 | Wikipedia |
| telluric acid               | Te(O)6  | Te(O)6  | mp-626012 | 0.050             | 2.23  | 5.28            | 136.0  |       | Wikipedia |
| trioxotetrafluoroditelluric acid | TeH2O3F4 | H2TeO3F4 | mp-119134 | 0.0               | 4.62  | 7.89            | -      |       | [47]   |
| tellurium hexafluoride      | TeF6    | TeF6    | mp-1875   | 0.0               | 4.40  | 2.47            | -38.9  | -37.6 | [47]   |
| titanium tetrabromide       | TiBr4   | TiBr4   | mp-569814 | 0.0               | 2.84  | 2.78            | 39.0   | 230.0 | Wikipedia |
| titanium tetrachloride      | TiCl4   | TiCl4   | mp-30092  | 0.0               | 3.47  | 2.52            | -24.1  | 136.4 | Wikipedia |
| tungsten hexachloride       | WC6f    | WC6f    | mp-571518 | 0.0               | 1.92  | 4.94            | 275.0  | 346.7 | Wikipedia |
| xenon tetrafluoride         | XeF4    | XeF4    | mp-23185  | 0.0               | 2.86  | 3.48            | 117.0  |       | Wikipedia |

TABLE II: Additional materials found by graph-theoretical approach. All information is as in Table S1.
| formula            | MP-ID  | binding energy | volume | HOMO  | LUMO  | dipole |
|--------------------|--------|----------------|--------|-------|-------|--------|
| Sb4O6              | mp-1999| -4.52          | 170.94 | 2.92  | 4.09  | 0.01   |
| As4S5              | mp-502 | -3.31          | 222.33 | 1.42  | 2.64  | 0.13   |
| As4S4              | mp-542846| -2.82       | 195.84 | 1.38  | 2.80  | 0.00   |
| As4O6              | mp-2184| -2.63          | 162.33 | 2.04  | 4.49  | 0.00   |
| P4O10              | mp-562613| -2.17        | 193.75 | 5.47  | 6.01  | 0.00   |
| Pt6Cl12            | mp-23290| -1.69          | 427.50 | 1.48  | 2.01  | 0.00   |
| Pd6Cl12            | mp-29487| -1.75          | 415.68 | 1.09  | 1.64  | 0.00   |
| Nb2I10             | mp-569578| -2.30         | 454.88 | 0.61  | 1.08  | 0.00   |
| As4Se4             | mp-542570| -6.78         | 208.38 | 0.85  | 2.17  | 0.00   |
| P4S10              | mp-541788| -2.94         | 346.68 | 2.17  | 2.97  | 0.00   |
| Ge4S6Br4           | mp-540792| -2.95         | 387.29 | 2.14  | 2.79  | 0.01   |
| Ge4S6I4            | mp-27928| -3.15          | 455.05 | 2.06  | 2.59  | 0.02   |
| Nb2Br10            | mp-28601| -6.58          | 368.70 | 1.37  | 1.70  | 0.00   |
| Ta2Br10            | mp-1203015| -4.74        | 372.00 | 1.86  | 2.19  | 0.00   |
| Nb2Cl110           | mp-23307| -3.87          | 315.41 | 2.07  | 2.33  | 0.00   |
| Ta2I10             | mp-570679| -8.72          | 459.17 | 0.94  | 1.41  | 0.00   |

**TABLE III:** Additional properties calculated using vdW-DF functional: Cluster formula, MP-ID, binding energy per cluster (eV), volume per cluster (Å³), HOMO and LUMO levels of cluster aligned w.r.t. vacuum level (eV), and dipole (eÅ).
FIG. 1: Band gap vs. high-frequency dielectric constant $\varepsilon_\infty$. Otherwise the same as Figure 1(b) in the main paper.
FIG. 2: Atomic structures for all materials included in Figure 1(c) of the main paper.
FIG. 3: Atomic structures for all materials included in Figure 1(d) of the main paper.
FIG. 4: Electronic structure of 0D clusters adsorbed on MoS\(_2\). Local density of states of the cluster and of MoS\(_2\) layer. Total DOS pristine MoS\(_2\) is given as a reference. All DOS are aligned using the vacuum level.
[1] Werner Lenhard, Harald Schäfer, Hans-Ulrich Hürter, and Bernt Krebs. Ein beitrag zu den koordinationsverhältnissen in den gasförmigen ma2cl8-komplexen das spektrum von coa2clm8–n und die kristallstruktur von pdal2cl8. Zeitschrift für anorganische und allgemeine Chemie, 482(11):19–26, 1981.

[2] Timothy J. Boyle, Nicholas L. Andrews, Todd M. Alam, David R. Tallant, Mark A. Rodriguez, and David Ingersoll. Speciation in the acl3/so2cl2 catholyte system. Inorganic Chemistry, 44(16):5934–5940, 2005.

[3] Harold J. Whitfield. Crystal and molecular structure of tetra-arсенic pentasulphide. J. Chem. Soc., Dalton Trans., pages 1740–1742, 1973.

[4] Silvia Haupt and Konrad Seppelt. Das arsenic oxide trichloride dimer. Zeitschrift für anorganische und allgemeine Chemie, 626(8):1778–1782, 2000.

[5] https://chemdb.net/en/compound/7JyenBPrd5/.

[6] Wolfgang Höne, Yuri Grin, Armin Burkhardt, Ulrich Wedig, Martin Schultheiss, Hans Georg von Schnering, Ralf Kellner, and Herbert Binder. Syntheses, crystal structures, and electronic structures of the boron halides b9s9(x=cl, br, i). Journal of Solid State Chemistry, 133(1):59–67, 1997.

[7] https://chemdb.net/en/compound/JEyw7sQyqe/.

[8] A. Benrath and B. Schiffer. Das system kobaltbromid-ammoniumbromid-wasser zwischen 0° und 100°. Zeitschrift für anorganische und allgemeine Chemie, 240(1):67–79, 1938.

[9] Kenji Waizumi, Hideki Masuda, and Hitoshi Ohtaki. X-ray structural studies of febr2-4h2o, cobr2-4h2o, ncl2-4h2o and cubr2-4h2o. cis/trans selectivity in transition metal(ii) dihalide tetrahydrate. Inorganica Chimica Acta, 192(2):173–181, 1992.

[10] Jan Rosdahl, Mikhail Gorlov, Andreas Fischer, and Lars Kloo. Syntheses and crystal structures of di- and trimercury chlorogallates. Zeitschrift für anorganische und allgemeine Chemie, 630(5):760–762, 2004.

[11] T. N. Srvastava, J. E. Griffiths, and M. Onyiszchuk. Derivatives of monogermande: Part ii. preparation and properties of germyl pseudohalides and related compounds. Canadian Journal of Chemistry, 40(4):739–744, 1962.

[12] A. B. Venediktov, S. V. Korenev, D. B. Vasil’chenko, A. V. Zadesenets, E. Yu. Filatov, S. N. Mamonov, L. V. Ivanova, N. G. Prudnikova, and E. Yu. Semitu. On preparation of platinum(iv) nitrate solutions from hexahydroxoplatinates(iv). Russian Journal of Applied Chemistry, 85(7):995–1002, 2012.

[13] Ralf Steudel, Klaus Bergemann, Jürgen Buschmann, and Peter Lugger. Large sulfur–nitrogen heterocycles: Preparation of the sulfur imides s_nh (n = 8, 9, 11) and structures of s8nh and s9nh. Angewandte Chemie International Edition in English, 35(21):2537–2539, 1996.

[14] https://www.webelements.com/compounds/chlorine/chlorine_nitrate.html.

[15] A. Lee Smith, William E. Keller, and Herrick L. Johnston. The infrared and raman spectra of condensed nitric oxide. The Journal of Chemical Physics, 19(2):189–192, 1951.

[16] Bernt Krebs, Holger Janssen, Niels J. Bjerrum, Rolf W. Berg, and G. N. Papatheodorou. Niobium aluminum chloride (nbalcl8): a molecular dinuclear complex in the solid, melt, and vapor phases. synthesis, crystal structure, and raman spectra. Inorganic Chemistry, 23(2):164–171, 1984.

[17] Neil Bartlett and James Trotter. The structure of the orthorhombic phase of osmium oxide pentafluoride, osof5. J. Chem. Soc. A, pages 543–547, 1968.

[18] T. E. Thorpe and A. E. Tutton. Xc.—phosphorous oxide, part ii. J. Chem. Soc., Trans., 59:1019–1029, 1891.

[19] Th. Kruck and K. Baur. Synthesis of tetrakis(trifluorophosphine)-platinum(0) and tetrakis(trifluorophosphine)-palladium(0). Angewandte Chemie International Edition in English, 45(6):521–525, 2006.

[20] https://www.lookchem.com/Phosphorus-oxybromide/.

[21] Philip Clare, Trevor J. King, and D. Bryan Sowerby. Crystal structures of cis-2,4,6-trichloro- and cis-2,4,6-tribromo-2,4,6-trifluorocyclotri(phosphazene). J. Chem. Soc., Dalton Trans., pages 2071–2074, 1974.

[22] P. M. Treichel, Ruth A. Goodrich, and S. B. Pierce. Synthesis and characterization of hpf4 and h2pf3. Journal of the American Chemical Society, 89(9):2017–2022, 1967.

[23] V. Kaiser and F. Menzel. Crystal structure of 2,4-bis(methylthio)-1,3-dithiaphosphetane-2,4-disulfide, (ch3s)2(p2s2)s2. Zeitschrift für anorganische und allgemeine Chemie, 630(5):760–762, 2004.

[24] Werner Storzer, Dietmar Schomburg, Gerd-V olker Röschenthaler, and Reinhard Schmutzler. Darstellung und strukturbestimmung von trans-bis(dichlorsulfan)platin(iv)-chlorid pdc12(scl2)2 und trans-bis(dichlorsulfan)palladium(ii)-chlorid pdcl2(scl2)2. Zeitschrift für anorganische und allgemeine Chemie, 588(1):69–76, 1990.

[25] V.B. Rybakov, L.A. Aslanov, S.V. Volkov, A.V. Grafof, V.I. Pekhn’o, and Z.A. Fokina. X-ray diffraction study of palladium (2) chlorochalcogenide complexes. Zhurnal Neorganicheskoy Khimii, 36(5):1197–1201, 1991.

[26] https://www.chemsrc.com/en/cas/13768-11-1_1195391.html.

[27] Christian Wagner, Frank Herzog, Jutta Knaudt, and Gerhard Thiele. Rus4cl12 und ru2s6cl16, zwei neue ruthenium(ii)-komplexe mit
[32] A. J. Blake and Z. Žák. Structure of disulphuryldifluoride at 100 K. Acta Crystallographica Section C, 49(1):7–9, Jan 1993.

[33] D. P. Stevenson and Robert A. Cooley. The structure of thionyl bromide. Journal of the American Chemical Society, 62(9):2477–2479, 1940.

[34] Jack G. Ballard, Thomas Birchall, and David R. Slim. Preparation of antimony(v) trichloride difluoride and its characterization by means of x-ray crystallography, antimony-121 mössbauer, and raman spectroscopy. J. Chem. Soc., Dalton Trans., pages 1469–1472, 1977.

[35] https://de.wikipedia.org/wiki/Diselendibromid.

[36] John C. Dewan and Anthony J. Edwards. Fluoride crystal structures. part 27. seleninyl difluoride at –35 °c. J. Chem. Soc., Dalton Trans., pages 2433–2435, 1976.

[37] K. W. Törnroos, G. Calzaferri, and R. Imhof. Octachlorosilasesquioxane, Cl₈Si₈O₂. Acta Crystallographica Section C, 51(9):1732–1735, Sep 1995.

[38] Cecil L. Frye and Ward T. Collins. Oligomeric silsesquioxanes, (hsio₃/2)n. Journal of the American Chemical Society, 92(19):5586–5588, 1970.

[39] Alois Haas, Reiner Hitze, Carl Krüger, and Klaus Angermund. Darstellung und charakterisierung von silithia- und silasela-grundkörpern / synthesis and characterisation of silithia and silasela basic compounds. Zeitschrift für Naturforschung B, 39(7):890–896, 1984.

[40] Maxim N. Sokolov, Artem L. Gushchin, Pavel A. Abramov, Alexandr V. Virovets, Eugenia V. Peresypkina, Svetlana G. Kozlova, Boris A. Kolesov, Cristian Vicent, and Vladimir P. Fedin. Synthesis and structure of silathia and silasela basic compounds. Russian Journal of General Chemistry, 72(10):1576–1585, 2002.

[41] Xiaoli Wang, Yanchao Wang, Maosheng Miao, Xin Zhong, Tian Cui, Jianfu Li, Li Chen, Chris J. Pickard, and Yanming Ma. Cagelike diamondoid nitrogen at high pressures. Phys. Rev. Lett., 109:175502, Oct 2012.

[42] K.S. Liang. Local atomic arrangement and bonding studies in amorphous as₂se₃–as₄se₄. Journal of Non-Crystalline Solids, 18(2):197–207, 1975.

[43] Siegfried Pohl, Ulrich Seyer, and Bernt Krebs. Sulphidhalogenide des germaniums: Darstellung und strukturen von ge₄sebr₄ und ge₄so₄ / thiohalides of germanium: Preparation and structures of ge₄sebr₄ and ge₄so₄. Zeitschrift für Naturforschung B, 36(11):1432–1443, 1981.

[44] Silvia Haupt and Konrad Seppelt. Solid state structures of ascl₅ and sbcl₅. Zeitschrift für anorganische und allgemeine Chemie, 628(4):729–734, 2002.

[45] Farhad Tamadon and Konrad Seppelt. The elusive halides vcl₅, moc₁₆, and rec₁₆. Angewandte Chemie International Edition, 52(2):767–769, 2013.

[46] Joanna Supel and Konrad Seppelt. Rhenium trichloride dioxide, reo₂cl₃. Angewandte Chemie International Edition, 45(28):4675–4677, 2006.