Computational Synthesis of Substrates and 2D Materials by Crystal Cleavage

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Crystal cleavage provides a process to create atomically smooth materials surfaces. To identify possible cleavage planes in periodic materials, we generate bonding networks for crystals from MaterialsProject with five or fewer atoms in the primitive unit cell. For three-dimensional crystals, we systematically break up to three bonds in the bonding network. Successful cleavage reduces the bonding network to two periodic dimensions, creating a layer of the cleaved crystal. We identify 3,897 unique cleavage surfaces across 1,847 crystals and characterize the likelihood of cleavage by calculating the work of adhesion and the relaxed surface energy of these layers using density functional theory to discover 2,924 potential substrates. We discuss the distribution of lattice parameters across these substrates and epitaxially match them against BaSnO₃. Following, we identify distinct trends in the work of adhesion of these layers and relate them to metallic and covalent/ionic bonding. For the lowest energy surfaces, we fully optimize the structure, including dispersion interactions, and identify 17 2D materials with surface energies below that of freestanding SnSe.

Single-crystal substrates are used for the epitaxial growth of crystalline thin films based on the similarity of their surface in terms of lattice parameters and symmetry. Many single-crystal substrate materials are commercially available with different surface orientations. However, while exfoliated 2D materials such as graphene are naturally smooth, cleaving a crystal does not guarantee a smooth surface. If there is energetic instability in the facet cut, various defects can form that limit the quality of the substrate for synthesis efforts. Hence, there is a need to identify new substrate materials. An example is the cubic perovskite BaSnO₃, which has suppressed electronic properties due to mismatch between the lattice parameters of itself and suitable substrates for growth.

The discovery of two-dimensional (2D) materials presents similar challenges to substrates, most notably that both require materials with low surface energies. Computational efforts to discovery novel 2D material have significantly increased the list of potential monolayers and helped guide experimental synthesis. One discovery technique is data mining, which searches bulk materials databases for yet unidentified monolayers. A recent effort in this direction identified and characterized the bonding network of a crystal structure using the topological scaling algorithm (TSA). This algorithm identifies bonding clusters within a finite number of unit cells, then uses the scaling of this network size as a function of supercells to define dimensionality and was used to discover over 600 low-energy 2D materials.

Alternative methods of identifying 2D materials include chemical substitutions on known structures and the ab-initio search for novel 2D crystal structures. These methods have successfully predicted 2D materials that were subsequently synthesized experimentally. The advantage of genetic algorithms over data mining and chemical substitutions approaches is that they do not rely on known crystal structures. However, genetic algorithm structure searches are computationally more expensive than data mining and chemical substitutions.

In this work, we present another approach to identify novel substrates and 2D materials, which utilizes crystal cleavage of bulk materials. This effort is motivated by our recent 2D structure search using the genetic algorithm software GASPro for the Ga₂O₃ system. In that search, we identified a monolayer structure that can be cleaved from the bulk crystal and was already experimentally synthesized. Thus, we use data mining techniques to discover planes of cleavage in fully periodic crystals. Rather than identifying van der Waals gaps, we propose to systematically break bonds in a crystal structure to create a layered, sub-periodic structure. When the breaking of bonds generates a layered structure, we extract a single monolayer and calculate the work of adhesion, i.e., the energy cost required to cleave the crystal and form two surfaces, using density functional theory. From this process, we identify a nearly 3,000 potential substrates with surface energies comparable to current substrates and 17 2D materials with formation energy comparable to freestanding SnSe.

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FIG. 1. An example of a cleavable crystal, YAgTe₂. The algorithm identifies four possible cleavage planes with low bond density resulting in substrates or single-layer materials.

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Candidate materials. For our study, we select all materials in the MaterialsProject database with five or fewer atoms in the primitive unit cell and which are within 50 meV/atom of the convex hull, the latter to promote thermodynamic stability. Next, the topological scaling algorithm (TSA) identifies conventionally networked structures and creates a list of all bonds between neighboring atoms for each of these structures. The bonding identification utilizes the atomic radii of the elements, which we obtained by increasing the value provided by the pymatgen software package by 10%.

Bond cleavage. We systematically break unique bonds up to a maximum number of bonds given by,

$$N_{\text{bonds}} = \text{round}\left(\alpha N_{\text{atoms}}^{2/3}\right)$$

where \(N_{\text{atoms}}\) is the number of atoms in the primitive cell, and \(\alpha\) is a scalable parameter based on the desired maximum number of bonds broken. The exponent of \(2/3\) appropriately scales the number of bonds per plane with increasing cell size. The choice of \(\alpha = 1\) in this work results in one to three cleaved bonds for unit cells of one to five atoms. It is worth noting that \(\text{Ga}_2\text{O}_3\) was not identified as cleavable by this search, as (i) the number of atoms in the primitive cell of the crystal is greater than five and (ii) the TSA identifies the crystal as layered when using our choice of 1.1 times the atomic radii of Ga and O.

Topology of resulting structure. To determine if a cleavage surface has been generated, the TSA is run on the primitive cell with \(N_{\text{bonds}}\) or fewer bonds broken, then a supercell. For each bond broken in the primitive cell, all periodic images of this bond in both the primitive cell and supercell are also broken. If the structural motif after bond breaking is identified as two-dimensional, and is the same stoichiometry as the overall cell, we have created a monolayer structure. This is then isolated and oriented such that the \(\vec{a}\) and \(\vec{b}\) lattice vectors span the 2D lattice of the monolayer structure and the \(\vec{c}\) lattice parameter is chosen perpendicular to the \((\vec{a}, \vec{b})\) plane.

Characterization of cleaved materials. To calculate the stability of the cleaved 2D materials, we perform density functional theory (DFT) calculations with the projector-augmented wave (PAW) method as implemented in the VASP package. We employ the Perdew-Burke-Ernzerhof (PBE) and vdW-DF-optB88 approximations for the exchange-correlation functionals, the latter being used to determine the role of dispersion interactions on the stability of the monolayers. To obtain convergence of the energy of the materials to 1 meV/atom, we use a \(\Gamma\)-centered \(k\)-point mesh with a density of 60 \(k\)-points per \(\AA^{-1}\) and a cutoff energy for the plane-wave basis set of 600 eV for all calculations. For the 2D materials, we employ a vacuum spacing of 14 \(\AA\) for the PBE calculations and further increase the vacuum spacing to 20 \(\AA\) for the dispersion corrected vdW-DF-optB88 functional. The DFT calculations are performed spin-polarized with an initial ferromagnetic configuration. Transition metals are initialized with a magnetic moment of 6 \(\mu_{\text{Bohr}}\) and all others atoms with a moment of 0.5 \(\mu_{\text{Bohr}}\).

Workflow. We use the software packages pymatgen and MPInterfaces to prepare the input files and analyze the results for the cleavage algorithm and the DFT calculations of the energetics and electronic structure. To improve the efficiency of the materials screening for the large number of candidate cleaved materials, we perform the structure relaxation in two steps. We initially relax each structure for a maximum of ten ionic steps, though not all extracted layers required that many steps for convergence. For the resulting lowest energy materials, we further relax the structure and analyze their stability and electronic properties.

Predicted substrates. From a starting set of 120,612 materials in the Materials-Project database, 1,847 crystals met the criteria of exhibiting (i) a primitive cell of 5 or fewer atoms, (ii) a bonding network of three-dimensional topology, and (iii) an energy within 50 meV/atom of the thermodynamic hull. For these 1,847 crystals, we identified 3,897 cleavage surfaces and extracted monolayers for each case. 1,834 bulk precursors phases successfully underwent structural optimization, from which 3,568 monolayers remained structurally intact and changed by less than 40% in surface area. The surface area change is used to screen systems that failed when optimizing in some way, typically due to forces in the system causing an expansion of the surface area that artificially lowers the surface energy of the monolayer.

Figure 2 compares the calculated work of adhesion and surface energy after partial optimization for the 3,568 cleaved monolayers. We observe that the work of adhesion is a reasonable indicator of the thermodynamic stability of these surfaces, with 1,759 materials displaying surface energies within 10% of their work of adhesion and 1,127 within 5%. Our search identifies several surfaces that are currently used as substrates, which include (0001) CdS, ZnO, and AlN. The light blue region in Fig. 2 highlights 2,924 surfaces with a

![Figure 2](image-url)
work of adhesion below that of (0001) AlN, and 459 surfaces fall below that of (0001) CdS. To identify novel freestanding monolayers, we fully optimize a subset of these structures, using a surface energy cutoff of 16 meV/Å², which was previously suggested for freestanding 2D materials.27

Figure 3 illustrates the distribution of the number of cleaved bonds and surface energies across the 3,496 of the cleaved monolayer materials. The joint distribution in Fig. 3(a) indicates that our cleavage criterion of Eq. (1) results in both a low density of cleaved bonds and a moderate spread of work of adhesion. Furthermore, the distribution indicates two clustering trends in the plot, which correspond to different average bond energies. We attribute these trends to different types of chemical bonds being broken. Metallic systems typically display high coordination numbers and somewhat lower bond energies. Covalent and ionic bonds share localized electrons, which results in lower coordination numbers and higher energies per bond. To test this hypothesis, Figures 3(b) and (c) show the work of adhesion and bond density distribution for monolayers derived from metallic and insulating precursors, respectively, based on the bandgap reported in the Material-sProject database. We observe that the two clusters in the distribution do correspond predominantly to metallic and covalent/ionic bonding with average bond energies of 1.1 and 2.2 eV/bond. Note that precursors without a bandgap entry in MaterialsProject are not included in Figs. 3(b) and (c).

To determine the potential of our data mining approach to expand the set of known substrates, we characterize the symmetry and lattice parameters of the cleavage surfaces. Figure 4 illustrates the lattice parameter distribution of the square, tetragonal, and hexagonal surfaces. The large number of substrates for each symmetry and the broad range of lattice parameters indicate that these cleaved crystals could act as substrates for a variety of thin-film systems. As an example, we epitaxially match cubic perovskite (100) BaSnO₃, using the crystal structure and stiffness tensor provided by MaterialsProject, to substrates with a work of adhesion below that of (0001) AlN. We use the pymatgen lattice matching algorithm to epitaxially match the perovskite to the layers extracted in our search, matching to only a single unit cell of BaSnO₃. We identify 46 layers when using the screening criteria of (i) a work of adhesion less than 200 meV/Å² and (ii) a strain energy less than 1 meV/atom. We here highlight one potential substrates, the (001) surface of the oxide Rb₂NiO₃. The (001) cleavage of this oxide requires a small work of adhesion of 20 meV/Å². The resulting epitaxial strain of BaSnO₃ is only 0.3% and corresponds to a strain energy of 0.21 meV/atom, indicating the opportunity for defect-free growth of BaSnO₃ on this substrate.

Dispersion interactions. We fully optimized the structure of 115 monolayers and observed that several of them display...
energy, on average increasing surface energy by 11 meV/Å.

Results for 2D materials. To determine the stability of the monolayers and their potential as free-standing 2D materials, we fully relax their structure with the dispersion corrected vdW-DF-optB88 functional. We observe that nearly all cleavage surfaces have a significant vdW component to the energy, on average increasing surface energy by 11 meV/Å². With systems of fewer electrons, such as Na and K, the increases were lower.

Our search identifies 17 2D materials with surface energies below 16 meV/Å², 15 of which were not reported in the previous search for 2D materials using the TSA. Figure 5 shows the band edge positions of the 17 cleaved monolayers. We observe a wide range of electronic properties in these 2D materials. Surprisingly, Na and K appear in the search, in 3 and 4 atom monolayers with surface energies within 1 meV/Å² of each other and nearly identical work functions. The LiCl, ClBr, ClI, BrI, and IBr covalent bonded layers are all found to have large bandgaps, ranging from 5 to 6 eV. These 2D materials have an identical crystal structure, shown in Fig. 6, and are not reported in either MaterialsWeb or the Computational 2D Materials Database. CuI and AgI exhibit the same crystal structure, and PbS and TII display a non-buckled form of this structure.

In conclusion, we applied a topological scaling algorithm that systematically breaks bonds in three-dimensional crystals to identify cleavage planes. We identify 3,897 unique cleavage surfaces across 1,834 periodic crystals and determine their structure and stability. 2,924 surfaces display a work of adhesion comparable to that of the known substrate material, (0001) ALN. These cleavage surfaces show a broad distribution of symmetries and lattice parameters. We illustrate their utility by identifying substrates that are epitaxially well matched to BaSnO₃. We also discover 17 monolayers that meet the surface energy criterion of free-standing 2D SnSe, and identify a set of 2D materials, LiI₂X₂(001) [X=Cl, Br, I, IBr], which are not listed in MaterialsWeb.

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