

Understanding principles of phase stability for experimental synthesis of 2D electrides

Motivations:

Layered electrides are exotic materials possessing bare-electrons that do not occupy any atomic orbital, and accordingly, their crystal structures consist of positively charged atomic slabs with delocalized electrons between slabs. This novel structural motif leads to a class of low work function compounds that are as conductive as silver; however, proposed applications as memristors, catalysts, and solid-state dopants can only be explored when free-electrons are exposed at the surface. To this end, 2D electrides have attracted considerable computational interest, but thus far, there remains no method to grow 2D electride films. Although standard synthetic strategies will fail due to 2D electride instability, my preliminary calculations¹ suggest that transfer of electrons from electride to substrate could actually stabilize the resulting film. By combining charge-transfer with a thorough investigation of the phase diagram at low dimensionality and elastic interactions with the substrate, the first electride film can be produced (Figure 1). **Thus, I propose a phase-stabilization strategy towards synthesis of layered electride thin films via chemical vapor deposition (CVD). Conventional epitaxy will be combined with novel charge-transfer stabilization to synthesize electrides that are otherwise inaccessible, even in bulk form.**

Using a model electride (Ca_2N) to understand the underlying principles and verify my synthetic approach, my proposal has the following goals:

- (1) **Computationally investigate phase stability** via (a) 2D Ca-N phase diagram prediction and (b) substrate epitaxial and charge-transfer stabilization, which will illuminate the fundamental surface chemistry and enable a reasonable synthetic approach.
- (2) **Experimentally synthesize a Ca_2N thin-film** via CVD to evaluate guiding principles for electride phase stability and to grow the first 2D electride film.
- (3) **Generalize the CVD synthetic approach** for other predicted electride materials to initiate a new field of superconductive, low work-function films

Research Plan:

(1a) *Determine all competing phases for the thin-film Ca-N system:* I have successfully reproduced the known phase diagram for the bulk Ca-N system by implementing a DFT-driven phase-space search algorithm (CALYPSO). However, bulk phases and corresponding enthalpies may not accurately represent the thin-film structure, as is true for well-known systems like silicon. That is, the preferred structure in bulk may be the layered electride whereas another phase is favored in an atomically thin system. By identifying the competing 2D phases, I can accurately quantify the electride metastability. **Therefore, I will use an extension of the CALYPSO package to predict the 2D phase system, which I will use to demonstrate how the Ca-N phase diagram changes with material dimensionality and anticipate synthetic challenges for phase purity.**

(1b) *Identify substrates that favor the layered electride through phase stabilization:* In addition to dimensionality, the stability of a Ca_2N thin film will largely depend on the substrate epitaxial

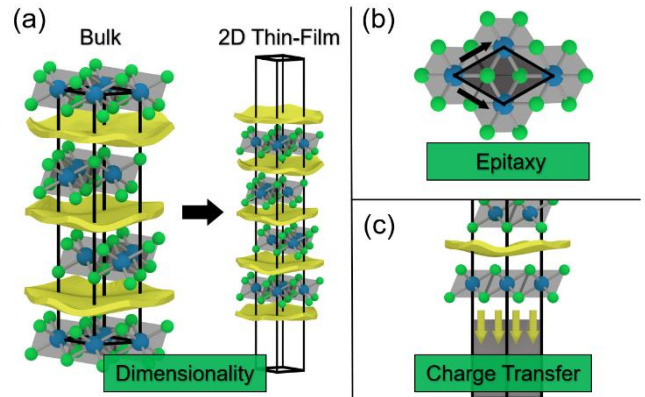


Figure 1. The three major influences (a, b, c respectively) of phase stability examined in this proposal. The unit cell of a layered electride (Ca_2N) depicts $[\text{Ca}_2\text{N}]^+$ atomic slabs (Ca^{2+} = green; N^{3-} = blue) and free-electrons (yellow).

match/strain and charge transfer. Using DFT-calculated elastic tensors and a data-mining package (PyMatGen) to match numerous substrate faces with those of a target film, I have written a script to identify the smallest common unit cell area of each pair and calculate the strain energy associated. Here, both the coincident interfacial area and strain energy will be minimized for the film's target phase and maximized for competing phases. This approach has resulted in the syntheses of metastable phases < 75 meV/atom above hull.² Further, the massively electron-donating character of the electride toward a substrate will provide added stabilization of the layered structure as I have found significant bonding character across the interface relative to standard films.¹ Should this donor-acceptor (electride-substrate, respectfully) character be exploited to stabilize the layered electride, I expect that phases >150 meV/atom above hull will become experimentally accessible. ***Thus, a comprehensive comparison of competing Ca-N phases (step 1a) with epitaxy/charge-transfer stabilization will be used to favor the layered electride phase, making this analysis instrumental towards understanding stability of the electride thin film.***

(2) ***Synthesize a Ca₂N thin film by CVD and validate the charge-transfer stabilization effect:*** while kinetic and stoichiometric control (via carrier gas and precursor partial pressures) is universal among CVD systems, standard commercial instruments do not possess high-purity load/lock systems to prevent oxidization. To address this issue, I have built a custom system and ensured the proposed reaction conditions can be employed. Thus far, I successfully synthesized an extremely reactive electride (Sr₂N) as a phase pure bulk material, and I have begun experimental syntheses of the less-reactive Ca₂N thin film. Further, the effect of epitaxy and charge transfer can be scrutinized by means of exemplary substrates identified in step 1b. I will do this by comparing substrates that achieve (i) optimal epitaxy but no charge transfer, (ii) optimal epitaxy and charge transfer, and (iii) no epitaxy but optimal charge transfer. ***Together, the combined approach of predictive phase-stabilization with a specialized CVD system will yield the first successful synthesis of an electride film and will evaluate the novel charge-transfer stabilization effect.***

(3) ***Extend the synthetic approach used for Ca₂N to other target electride systems:*** in addition to experimentally known layered electrides (Sr₂N, Ba₂N, & M₂C; M = Y, Gd, Tb, Dy, Ho), there are also many layered electrides that have been proposed via DFT but never synthesized, even in bulk form. For example, attempts to synthesize Sr₂P, a layered electride that is 150 meV/atom above hull, instead formed the more stable phase, Sr₅P₃. However, by exploiting the principles I develop above – interfacial charge transfer and epitaxy – I will grow the Sr₂P layered electride phase as a thin film. Likewise, this approach will be employed for other metastable layered electrides that are inaccessible via bulk compounds. ***By examining known and predicted layered electrides, I will produce a new class of films toward catalytic, doping, and electronic applications and further generalize the phase-stabilization principles identified with Ca₂N.***

Added Intellectual Merit & Broader Impacts:

Not only does this proposal advance the field of surface chemistry and novel thin films, but it also serves as a key model in the design of other 2D materials. ***This work will be the first complementary usage of phase space discovery and substrate epitaxy/charge-transfer data mining.*** Here, I will provide a new strategy to grow metastable materials previously inaccessible, serving as an outline for others to do the same and guiding syntheses of novel materials in the broader materials community. As an NSF fellow, I will carry out this proposed work to provide a greatly needed synthesis for electride thin-films as well as report a thorough computational approach applicable to many material systems.

References: (1) Woomer, A. H; Druffel, D. L.; Sundberg, J.D.; Pawlik, J.T.; Warren, S.C. *under review* (2) Ding, et. al. *ACS Appl. Mater. Interfaces* **2016**, 8, 13086.