Upper-Bound Energy Minimization to Search for Stable Functional Materials with Graph Neural Networks

Jeffrey N. Law, a Shubham Pandey, b Prashun Gorai, a,b,c Peter C. St. John a,c

The discovery of new materials in unexplored chemical spaces necessitates quick and accurate prediction of thermodynamic stability, often assessed using density functional theory (DFT), and efficient search strategies. Here, we develop a new approach to finding stable inorganic functional materials. We start by defining an upper bound to the fully-relaxed energy obtained via DFT as the energy resulting from a constrained optimization over only cell volume. Because the fractional atomic coordinates for these calculations are known a priori, this upper bound energy can be quickly and accurately predicted with a scale-invariant graph neural network (GNN). We generate new structures via ionic substitution of known prototypes, and train our GNN on a new database of 128,000 DFT calculations comprising both fully-relaxed and volume-only relaxed structures. By minimizing the predicted upper-bound energy, we discover new stable structures with over 99% accuracy (versus DFT). We demonstrate the method by finding promising new candidates for solid-state battery (SSB) electrolytes that not only possess the required stability, but also additional functional properties such as large electrochemical stability windows and high conduction ion fraction. We expect this proposed framework to be directly applicable to a wide range of design challenges in materials science.

1 Introduction

Overcoming critical barriers in materials science will require the discovery of yet unknown structures with precisely tailored properties. Computational searches driven by quantum chemistry calculations have accelerated materials exploration over large compositional and structural spaces, but are still limited to few tens of thousands of materials.1–4 Often, such searches are restricted to structures previously documented in crystallographic databases such as the Inorganic Crystal Structure Database (ICSD)5 and Cambridge Structural Database (CSD),6 which predominantly comprise experimentally synthesized inorganic materials. Their use in discovery campaigns for novel materials is therefore limited. Solid-state batteries (SSBs) are one such application, where the use of solid electrolytes makes SSBs safer and more energy dense than traditional Li-ion technology. SSBs require materials that meet several performance metrics,7 and remain limited by the thermodynamic instability of electrode-electrolyte interfaces.8,9 For instance, well-known solid electrolytes such as Li10GeP2S12, Li3PS4Cl (argyrodite), and Li2La3Zr2O12 decompose at the interface with Li-metal anode forming solid-electrolyte interphases that are difficult to control and cause performance degradation.10,11 Therefore, further improvements to SSB design require searching for new materials that are stable at suitable reduction and oxidation potentials.

A central problem in using machine learning (ML) methods to accelerate the search for novel crystal structures is finding structures that are thermodynamically stable, i.e., stable against decomposition into competing phases. Compositional models are not sufficiently accurate to reliably predict thermodynamic stability.12,13 Graph neural network (GNN) models have achieved impressive results in predicting formation energy and decomposition energy with mean absolute error (MAE) close to chemical accuracy (0.03-0.05 eV/atom).14–17 However, GNN models require the crystal structure as inputs, which are available only after performing expensive DFT relaxations. A considerably harder problem is predicting a priori whether a hypothetical crystal structure input will be stable before performing DFT relaxation. Recent studies have made some progress in this direction through the use of scale-invariant approaches, where the volume of input structures is normalized to make GNN models less sensitive to volume changes that often occur during relaxation.18,19 It has been previously shown that including high-energy structures as training data is critical to developing models intended to rank the stability of potential crystal structures for a given composition.13 Analogously, training GNN models only on fully-relaxed structures and their DFT total energies may bias the models to under-predict the energies of high-energy structures in unfavorable arrangements.

In this work, we develop a generalized approach for finding new inorganic crystal structures that are likely to be stable. We first demonstrate that the success of scale-invariant approaches in predicting the DFT-relaxed total energy of a crystal structure depends heavily on the degree to which the structure relaxes away from the initial unrelaxed structure. In a wide search over structures created by ionic substitution,21 DFT often alters the initial structures drastically during relaxation to a local energy minimum. Predictive models for energy trained with these unrelaxed structures as inputs are therefore inaccurate and unsuitable for screening potentially stable decorations. We present an alternate approach to finding new stable structures over a large decoration space that is compositionally and structurally diverse. First, we construct a database of constrained DFT relaxations over only the unit cell volume, which by design yields an upper bound

1 National Renewable Energy Laboratory, Golden, CO 80401, USA. 2 Colorado School of Mines, Golden, CO 80401, USA. 3 E-mail: jeffrey.law@nrel.gov, pgorai@mines.edu, peter.stjohn@nrel.gov
to the total energy of the unconstrained (full) relaxation. This upper-bound energy can be predicted to a high accuracy by scale-invariant ML models (MAE $\sim 0.05$ eV/atom), since fractional coordinates in the unit cell are known precisely. By subsequently searching for decorations that minimize this predicted upper-bound energy, we find novel crystal structures that are highly likely to be stable. Out of 14.3 million decorated structures, this approach predicted a stable structure for 2,003 compositions. Validating these top candidates with DFT confirmed $> 99\%$ of them to be thermodynamically stable i.e., having negative decomposition energy. We find many of these stable candidates also have suitable functional properties for SSBs, with structural similarities to previously explored solid electrolytes, electrodes, and coatings. Expanding our search to an even larger number of compositions and prototypes will exponentially increase the search space, making it computationally intractable to exhaustively assess the stability of every structure. To address this future need, we demonstrate a reinforcement learning (RL)-augmented search strategy that finds stable structures using our surrogate stability function at a fraction of the computational cost. Overall, this study shows that ML strategies are able to drastically reduce the computational cost and time to find promising inorganic functional materials.

## Results and Discussion

### 2.1 Challenges in Predicting Thermodynamic Stability

To be useful in screening candidate structures for stability, a machine learning (ML) surrogate model must be able to predict the total energy of a relaxed structure using only information available before the relaxation is performed. To provide our surrogate model with relevant training examples, we first constructed a database of example hypothetical structures through ionic substitution with compositions suitable for SSBs. We selected $67,489$ candidate structures for full DFT relaxation by decorating prototype ICSD structures with new compositions (Section 3.3.2). We refer to this as the fully-relaxed dataset. The corresponding total energies in this dataset are denoted by $E_{\text{tot}}$.

We first trained a scale-invariant GNN model (Section 3.1) on the ICSD and fully-relaxed datasets, where we paired the unrelaxed structures with their corresponding total energy after relaxation. We withheld $\sim 5\%$ of structures in each dataset for the validation and test sets. While the model performed well on ICSD structures (gray points in Figure 1c, MAE $= 0.05$ eV/atom), we found that the error was much larger on the fully-relaxed dataset (orange points in Figure 1c, MAE $= 0.13$ eV/atom). The higher MAE for the fully-relaxed dataset is likely due to many of the input structures starting in highly unfavorable configurations, such that DFT relaxation significantly alters their volume, cell shape geometry, and fractional atomic coordinates in finding a local energy minimum.

To quantify the structural change during DFT relaxation, we computed the cosine distance between the unrelaxed and relaxed structure pairs using Matminer fingerprints (see Section 3.4). Here, a cosine distance of zero indicates high structural similarity, ignoring any volume changes. With our wide range of prototypes and decorations, we found that over $86\%$ of pairs had a cosine distance above 0.1, meaning the vast majority of structures change quite dramatically after relaxation (Figure 1b). This is in stark contrast to the distribution of distances for structures in the Open Quantum Materials Database (OQMD) (Figure 1a), where similar GNN models are able to achieve high accuracy for unrelaxed structures i.e., MAE $< 0.05$ eV/atom. This result implies that while scale-invariant methods are robust to changes in the cell volume during DFT relaxation, they cannot account for large changes in fractional coordinates and cell shape geometry when DFT relaxes a structure far away from a high-energy starting configuration.

### 2.2 Volume-only Structure Relaxations

Rather than attempt to directly predict the energy resulting from a full DFT relaxation, we developed an alternate approach. We noticed in our fully-relaxed dataset that when a prototype decoration was favorable for a new composition, the structure tends
**Fig. 2** Overview of approach and dataset generation. (a) Starting from an unrelaxed structure, we predict an upper bound for the total energy i.e., energy after a constrained relaxation. We then evaluate the thermodynamic stability relative to competing phases and prioritize structures predicted to be stable, meaning the upper bound of the decomposition energy is $< 0$ eV/atom. If the decomposition energy upper bound is $> 0$ eV/atom, the structure could still be stable after full relaxation. (b) Our element library consists of conducting ions ($C$), framework cations ($F$), and anions ($A$). We build valence-balanced compositions of the general form $C_xF_yA_z$, where $x$, $y$, and $z$ are the stoichiometries corresponding to $C$, $F$, and $A$, respectively. Here, $i$ and $j$ are 1–2 i.e., we consider up to 2 framework cations and 2 anions. For a given composition, we decorate the elements in prototype structures (from a prototype library) via ionic substitution. These structures are then relaxed with DFT in two ways: (i) full relaxation, and (ii) volume-only relaxation, where the cell shape and atom positions are held constant.

The success of scale-invariant GNNs in previous applications suggests that the optimal volume and energy for a given structure can be predicted by its fractional coordinates and cell shape geometry. By constraining these features during a volume-only relaxation, we are able to augment our training set with high-energy examples, and provide a better foundation to distinguish favorable from unfavorable structure decorations. The volume-relaxation also provides us with an accurate upper bound to the total energy calculated by the unconstrained relaxation, since the energy must stay the same or decrease when DFT is allowed to fully relax the structure. Note that this upper bound is not a theoretical limit to the total energy of the structure, but serves as a useful reference point. While searching for stable structures in a large decoration space, if a volume-relaxed structure is not predicted to be stable w.r.t. competing phases, the fully-relaxed structure may or may not be stable. However, if a volume-relaxed structure is stable, the fully-relaxed structure will be stable as well. Assuming at least some of the volume-relaxed structures are stable, we can efficiently screen for them in the unrelaxed decoration space using an accurate surrogate model (Figure 2a).

We performed a volume-only relaxation on each of the ~68,000 unrelaxed structures used as inputs to the fully-relaxed dataset.
We pruned 7,000 that did not pass quality control filters (Section 3.3.4) and refer to these ~58,700 structures as the volume-relaxed dataset (Figure 2b). Figure 3a shows the differences in total energy between the two datasets, which confirms that the volume-only relaxations are indeed an upper bound.

With the addition of the volume-relaxed dataset, we trained a scale-invariant GNN on all three datasets (Figure 2b), this time using the relaxed geometry for the fully-relaxed structures instead of their input geometry. The prediction accuracy for all structures improved substantially (Figure 3b), as the GNN had access to the correct fractional coordinates for all inputs. Learning curves of the prediction error as a function of the dataset size show the model benefits from additional data up to the full dataset size (Figure 3c).

### 2.3 Surrogate Model Predictions

With the trained GNN surrogate model, we predicted the upper bound energy of all 14.3 million possible decorations (Section 3.2). We estimated the thermodynamic phase stability of each of these structures by computing their decomposition energy obtained through a convex hull analysis. Here, the convex hull is constructed by considering competing phases from the ICSD. The total energy of ICSD structures is taken from the NREL Materials Database,\textsuperscript{23} as explained in Section 3.3.3. The decomposition energy ($E_{\text{decomp}}$) is a measure of the thermodynamic stability of a structure against chemical decomposition into competing phases.\textsuperscript{12} $E_{\text{decomp}}$ is the minimum energy that the formation energy of an unstable material has to be lowered (more negative) before it becomes stable. Similarly, for a stable compound, $E_{\text{decomp}}$ is the maximum energy that the formation energy can be increased (less negative) before it becomes unstable.\textsuperscript{12} For each composition, we selected the structure with the lowest predicted energy. About 0.5% of compositions (2,003) had a structure with a negative $E_{\text{decomp}} < -0.1$ eV/atom. We applied this stringent cutoff on the $E_{\text{decomp}}$ to account for potential errors in the model predictions. Before analyzing these structures, we first validate the predicted stable structures with DFT.

### 2.4 DFT Confirmation of Predicted Stable Structures

We performed both full DFT relaxation and volume-only relaxation for the 2,003 predicted stable structures. Each of these 2,003 structures has a unique composition because we chose the lowest-energy structure for a given composition. Of the 1,707 structures where the DFT calculations successfully converged, we find the model predicts the energy upper bound i.e., volume-relaxed total energy, to a high accuracy (MAE = 0.045 eV/atom, Figure 4a). Nearly all predicted upper-bound total energies are larger than the fully-relaxed DFT energies (Figure 4b), consistent with our hypothesis that the volume-relaxed energies are an upper bound. We confirm that 99% (1,700 / 1,707) of the predicted structures are in fact stable, as determined from a convex hull analysis (Figure 4c). The DFT decomposition energies (calculated using fully-relaxed DFT total energy) are more negative i.e., more stable, than the predicted values, demonstrating the success of our upper-bound approach.

$E_{\text{decomp}}$ in Figure 4(c) are calculated from a convex hull construction by considering competing phases from the ICSD. However, to be self-consistent, the newly predicted stable structures should also be considered as competing phases. Therefore, we supplemented the ICSD structures with the 1,707 fully-relaxed structures as well as the lowest predicted energy for each of the ~220,000 compositions in our decoration space. Of these 1,707 compositions, 31 are found in the ICSD and therefore, are not considered further in our analysis. We reconstructed the convex hulls with this combined dataset and calculated what we term “self-consistent (SC) decomposition energy”. After this re-evaluation, 285 structures had a SC $E_{\text{decomp}} < 0$ eV/atom. We provide the structures, predicted, volume-relaxed, and fully-relaxed total energies, as well as the SC decomposition energies (see Section 3.5).

### 2.5 Novel Stable Structures

Thermodynamic stability is a prerequisite in the search for novel functional materials. Beyond stability, such materials must also exhibit specific functional properties. Our motivation for this study is to find new battery materials, which inspired our choice...
of chemistries to build the training dataset. We evaluate the suitability of the 285 newly predicted compositions/structures as solid-electrolytes in SSBs. For application in metal-anode SSBs, the solid electrolyte should have a low reduction potential i.e., close to 0 V w.r.t. Li/Li⁺. For compatibility with high-voltage cathode, the oxidation potential should be large, ideally > 4.0 V. In addition, a large electrochemical stability window (ESW) is desired. The volume fraction of the structure available to the conduction ions is a rough measure of the ionic conductivity, although more refined descriptors have been proposed. In summary, we sought structures with the following features: (F1) SC decomposition energy < −0.1 eV/atom, (F2) low reduction potential < 2.0 V w.r.t. Li/Li⁺, (F3) high oxidation potential > 4.0 V w.r.t. Li/Li⁺, (F4) large ESW > 2.0 V, and (F5) large volume fraction available to conduction ion ≥ 30%. These criteria (F1 – F5) represent a set of choices that can be easily adjusted for further analysis. Here, ESW is calculated as the difference between the oxidation and reduction potentials, which depend only on thermodynamic stability. While ESW calculated in this manner provides a useful guide, recent studies have highlighted the need to consider electronic band alignment between the electrolyte and electrodes to rigorously determine ESW. These band alignment calculations are computationally intensive and beyond the scope of our study.

Figure 5(b) shows the number of structures that pass each feature cutoff, as well as combinations of feature cutoffs. Structures that pass all cutoffs would be of particular interest. While we did not find any such structures that pass all feature cutoffs, several structures passed 3-4 cutoffs, as shown in Figure 5(b). Some of these structures and family of structures are labelled in Figure 5(b) and their DFT-relaxed crystal structures are shown in Figure 6.

A family of compounds with the general formulae CMₓX₇ (C = Li, Na; M = Sc, Y; X = halogens) are identified as stable structures that exhibit features F1 through F4, but are C-poor compositions, which contributes to their low conducting ion volume fraction. LiSc₂F₇ (Figure 6a, space group P2₁) and Li₂Br₇ (Figure 6b, space group Pnma) are two examples from the CMₓX₇ family of compounds. These structures are derived from the K and In rare-earth phyllochlorides, which feature unique seven-fold coordinated trivalent rare-earths. In the DFT-relaxed structures of LiSc₂F₇ and Li₂Br₇, shown in Figure 6, Sc and Y form edge- and corner-shared [ScF₇] and [YBr₇] polyhedra.

Li₂HfBr₆ (Figure 6c) and Li₂ZrBr₆ also pass the feature F1–F4 cutoffs. The predicted stable structures (space group R₃) contain isolated [HfBr₆] and [ZrBr₆] octahedra with interspersed Li. LiW₂Zn₄N₇ (Figure 6d, space group C2) forms a tetrahedrally-bonded structure consisting of edge-connected [ZnN₄] and [WN₄] tetrahedra. The structure is derived from Cu₄NiSi₂S₇, which crystallizes in monoclinic distorted sphalerite superlattice. NaLaP₄N₄ is yet another structure that fulfills F1–F4 cutoffs. The initial structure of NaLaP₄N₄ is created by decorating the BaSrFe₄O₈ trigonal (space group P31m) structure, with P occupying the tetrahedrally bonded Fe sites and La on the octahedrally-coordinated Sr sites.

LiHfSc₂Br₁₁ (Figure 6f) satisfies feature cutoffs F1, F2, and F4 and is derived from the NaZnZr₂F₁₁ structure (space group C2/m). [ScBr₄] octahedra are highly distorted while [HfBr₄] octahedra are less so. Li₂HfN₂ has a layered structure consisting of face-sharing [HfN₆] octahedra interspersed with Li (Figure 6g). Interestingly, Li₂HfN₂ is predicted to be stable at the interface with Li-metal anode (reduction potential 0.0 V), but stable only up to an oxidation potential of 1.2 V. It also has a high conducting ion volume fraction (0.41). Together, these features make Li₂HfN₂ a promising candidate for Li-anode coatings. In fact, Li₂HfN₂ is a hypothetical structure that is predicted to be stable in the Materials Project database and has been previously proposed as a candidate material for Li-anode coatings.

KSc₂₂ (Figure 6b) and KAlS₂ pass feature cutoffs F1 and F3–F5 and adopt the α-NaFeO₂ structure (space group R₃m). KSc₂₂ is thermodynamically stable with K-metal anode (reduction potential 0.0 V) and has an oxidation potential of 2.7 V. The layered
structure of KScS\textsubscript{2} lends itself to a high K ion volume fraction of 0.31 and possibly facile K\textsuperscript{+} ion diffusion. The layered Na\textsubscript{2}ZrO\textsubscript{3} (Figure 6i) and Na\textsubscript{2}HFO\textsubscript{3} also fulfill F1 and F3–F5 and possess the Li\textsubscript{2}SnO\textsubscript{3}-type structure (space group C2/c). Due to its layered structure, Li\textsubscript{2}SnO\textsubscript{3} has been studied as a promising cathode material.\textsuperscript{32} In fact, Na\textsubscript{2}ZrO\textsubscript{3} is predicted to be a stable structure in the Materials Project database.\textsuperscript{30} and Y-doped Na\textsubscript{2}ZrO\textsubscript{3} has been theoretically investigated as a Na-rich cathode material.\textsuperscript{33} We predict that Na\textsubscript{2}ZrO\textsubscript{3} should be stable against Na-metal anode, which is also confirmed by a phase stability analysis of the ternary Na-Zr-O chemical space on Materials Project.

Overall, we find that many of the 285 structures that are predicted to be stable contain group-3 (Sc, Y, La) and group-4 (Zr, Hf) elements. Most of the structures are halides, but we also find some oxides, halogenides, nitrides, and mixed-anion chemistries among the stable structures. The dominance of halides can be attributed to ionic nature of the compounds containing alkali elements (Li, Na, K) and halogens – a direct consequence of the large electronegativity differences between them. Valence-balanced ionic compounds tend to have high formation enthalpies and therefore, are generally stable. Furthermore, we observe that the cations in the predicted structures adopt their preferred coordination with anions e.g. Sc, Y, La in 6-fold coordination and 4-fold coordinated Zn in tetrahedral geometry.

2.6 Reinforcement Learning Optimization of Structures

Although in this study we were able to predict the stability of all 14.3 million decorated structures, other structure searches where a brute-force computation would be intractable require a more efficient approach. Examples include (i) cases where the prototype and composition libraries are much larger, leading to an explosion of potential decorated structures, (ii) a costlier evaluation function, and (iii) allowing decorated structures to go “off-prototype,” meaning structure parameters (e.g., cell shape, atomic positions) are allowed to change, leading to a potentially infinite search space. Here we demonstrate the use of Reinforcement Learning (RL) to improve the search efficiency in such applications.

RL, particularly methods based on a directed tree search such as Monte Carlo Tree Search (MCTS), enable precise control over the search space and function(s) to optimize. MCTS has previously been demonstrated to solve complex optimization problems on both organic\textsuperscript{34,35} and inorganic materials.\textsuperscript{36} We developed an action space for the crystal structure design problem based on the steps for generating a decorated structure through ionic substitution. We then implemented an MCTS optimization framework to find structures with desired properties, similar to the implementation by Sowndarya \textit{et al.} for designing organic molecules\textsuperscript{35,37} (see supplementary information). Following the approach of AlphaZero, this MCTS framework is augmented with a policy model that replaces the simulation phase (using a random policy) of MCTS with a predicted value score.

As AlphaZero was originally designed for competitive games, we used a ranked reward strategy to enable \textit{tabula rasa} self-play for the single-player combinatorial optimization problem.\textsuperscript{38} In this strategy, the final reward of a rollout is rescaled to 0 or 1 depending on whether the reward is greater than the 90\textsuperscript{th} percentile of the last 500 results. Thus, starting from an initially random walk over structure search space, the rollouts are guided by the policy to higher-reward structures.

To search for optimal candidate structures, we also imple-
We examined the improvement in efficiency for finding top candidate structures (i.e., predicted decomposition energy \(< -0.1\)) relative to the number of structures explored during the search. The largest improvement in efficiency was achieved during the beginning of the search; 34% of top-candidates were found after exploring 8% of decorations – a 4x increase relative to a brute-force search (Figure 7c). The reason the RL agent is unable to continually improve the reward and search efficiency may be because it exhausts branches of the search tree that are more densely populated with high-reward structures and is forced into continual exploration through generally low-reward spaces.

3 Conclusions

In this study, we have demonstrated an approach to finding stable, functional inorganic crystal structures by combining a GNN surrogate model with RL-based structural search. These results confirm the success of our upper-bound minimization strategy, where starting from a low-energy but unrelaxed starting point yields even lower energy stable crystal structures. We therefore rely on upper-bound optimization to find low-energy struc-
We demonstrate the method by searching for candidates for solid electrolytes, a demanding application that requires materials to simultaneously satisfy several competing criteria. Our method reveals 285 novel structures, many of which appear reasonable when compared with structures currently being explored for this application. Inspired by prior studies on ionic substitution, we constructed a library of prototype structures from the ICSD by first classifying them into composition types. Here, composition type is defined as the sorted stoichiometry that is agnostic of the element type. For example, structures with compositions $A_3B_1C_2$, $A_1B_2C_3$, and $A_1B_3C_2$ are categorized into the composition type “1-2-3”. The prototypes are limited to ordered (fully occupied lattice sites) and stoichiometric ICSD structures. At this stage, we also constructed a library of prototype structures from the ICSD by first classifying them into composition types. Here, composition type is defined as the sorted stoichiometry that is agnostic of the element type. For example, structures with compositions $A_3B_1C_2$, $A_1B_2C_3$, and $A_1B_3C_2$ are categorized into the composition type “1-2-3”. The prototypes are limited to ordered (fully occupied lattice sites) and stoichiometric ICSD structures. At this stage, we also...

**Acknowledgements**

We thank Vladan Stevanović for inspiring the creation of the structural prototype library. This work was authored in part by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the US Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. The information, data, or work presented herein was funded in part by the Advanced Research Projects Agency-Energy (ARPA-E), U.S. Department of Energy, under Award Number DE-AR0001205. P.G. also acknowledges support from NSF through award DMR-2102409. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.

**Conflicts of interest**

There are no conflicts to declare.

**Computational Methods**

**3.1 GNN Architecture**

We utilized a similar GNN architecture as was developed by Pandey et al. To input crystal structures to the model, each structure is converted into a graph where each atom site is a node and the 12 nearest sites of each atom in terms of raw distances (taking periodicity into consideration) constitute the edges. For node features, we use only the identity of the elements at each site, and for edges, we use the distance (in Å) between the two sites. We use six message passing layers in the GNN. One important difference from the GNN used by Pandey et al. is that we scale each structure such that the minimum distance between atoms is 1 Å, as was done in Pal et al. Thus, the model learns a scale-invariant version of the structures.

**3.2 Datasets**

Here we describe the prototype structures, the battery compositions, and how we decorated the prototype structures.

**3.2.1 Prototype Structures from ICSD**

Inspired by prior studies on ionic substitution, we constructed a library of prototype structures from the ICSD by first classifying them into composition types. Here, composition type is defined as the sorted stoichiometry that is agnostic of the element type. For example, structures with compositions $A_3B_1C_2$, $A_1B_2C_3$, and $A_1B_3C_2$ are categorized into the composition type “1-2-3”. The prototypes are limited to ordered (fully occupied lattice sites) and stoichiometric ICSD structures. At this stage, we also...
filtered out erroneous ICSD structures with multiple atoms occupying the same lattice site in a way that the total site occupation is larger than 1. The structures within each composition type were then de-duplicated by comparing their space groups and sorted list of Wyckoff site labels. With this procedure, we constructed a prototype library containing 4000 composition types spanning >13,000 structures.

### 3.2.2 Battery Compositions

Most well-known solid-state battery materials, including solid electrolytes and electrodes, are ternary and quaternary compounds with a distinct conducting ion (C), and a structural framework composed of cations (F) and anions (A). For example, the solid-electrolyte Li$_3$ScCl$_6$ structure contains Li$^+$ ions interspersed within a framework composed of [ScCl$_3$] octahedra. Therefore, we chose compositions of the general form $C_xF_yA_z$, where $x$, $y$, $z$ are the number of $C$, $F$, and $A$ per formula unit. For computational tractability, we limit the search to ternary, quaternary, and quinary compositions such that $x + y + z \leq 15$. To summarize, each composition is composed of 3-5 elements: (1) one conducting ion, $C$, (2) 1–2 framework cations, $F$, and (3) 1–2 anions, $A$. Informed by common battery chemistries, the battery elements and their oxidation states are chosen: (1) $C = \text{Li}^+$, $\text{Na}^+$, $\text{K}^+$, (2) $F = \text{Sc}^{+3}$, $\text{Y}^{+3}$, $\text{La}^{+3}$, $\text{Ti}^{+4}$, $\text{Zr}^{+4}$, $\text{Hf}^{+4}$, $\text{W}^{+6}$, $\text{Zn}^{+2}$, $\text{Cd}^{+2}$, $\text{Hg}^{+2}$, $\text{B}^{+3}$, $\text{Al}^{+3}$, $\text{Si}^{+4}$, $\text{Ge}^{+4}$, $\text{Sn}^{+4}$, $\text{P}^{+5}$, $\text{Sb}^{+5}$, and (3) $F = \text{F}^-$, $\text{Cl}^-$, $\text{Br}^-$, $\Gamma$, $\text{O}^-2$, $\text{S}^-2$, $\text{N}^-3$, $\text{P}^-3$. We only consider valence-balanced compositions in our search. In total, there are 220,824 valence-balanced compositions spanning 174 composition types.

### 3.2.3 Decorated Structures

For each composition, we generated decorated structures by considering all prototypes for the corresponding composition type (Section 3.2.1). For each prototype, we perform all possible decorations using ionic substitution where the elements in the prototype structure are replaced with the elements from the battery compositions (Section 3.2.2). We perform these substitutions following the stoichiometry. For example, if the battery composition is Mg$_2$ZrO$_4$ and the chosen prototype is BaAl$_2$S$_4$ (ICSD # 35136, space group $P6_3$), we substitute Al with Mg, Ba with Zr, and S with O in the structure. To keep the decoration space tractable, we do not perform decorations by Wyckoff sites and simply decorate all Wyckoff sites associated with an element with the substituting element. We also consider all possible stoichiometric combinations when performing the decorations. For example, the “1-2-4” composition type allows only one unique decoration while the “1-1-1-1” composition type accommodates 120 unique stoichiometric decorations on the same prototype structure. We also limit the search to prototypes with less than 50 atoms in the unit cell. We note that although $C_xF_yA_z$ compositions are inspired by the structure of well-known battery materials, we do not explicitly impose any bonding constraints (e.g., $F$ bonded to $A$) in constructing the decorated structures. In total, the 220,824 valence-balanced compositions result in 14.3 million hypothetical decorated structures.

### 3.3 Training Dataset

We train a surrogate GNN model to predict the total energy of a given structure. The thermodynamic stability can be evaluated from the DFT total energy through a convex hull construction. To train the GNN model, we selected a subset of hypothetical decorated structures for DFT relaxation to build a training dataset. Here, we describe the training datasets comprising ICSD and hypothetical structures, and the two types of DFT relaxations performed on the hypothetical structures.

#### 3.3.1 ICSD Structures

We used the same dataset of ICSD structures and their total energies as was used by Pandey et al.\textsuperscript{13}, which consists of ~14,000 structures available in the NREL Materials Database (NRELMatDB)\textsuperscript{23,43} as well as ~2,500 structures for which additional DFT calculations were performed.

#### 3.3.2 Decorated Structures for DFT Relaxation

We sampled a subset of the decorated structures (Section 3.2.3) to perform DFT calculations. For computational tractability, we sampled ternary, quaternary, and quinary compositions such that $x + y + z \leq 10$. With these constraints, there are 914 valence-balanced battery compositions spanning 72 composition types and 150,345 decorated structures. For each composition type, we randomly selected up to 10 compositions in way that every element accommodated by that composition type (condition of valence balance) are sampled. For each composition, we then consider all prototype structures (Section 3.2.3) in the corresponding composition type. We selected ~68,000 structures for full DFT relaxation and volume-only relaxation (Section 3.3.3).

#### 3.3.3 DFT Relaxations

DFT relaxations for the hypothetical structures were performed with VASP.\textsuperscript{44} Details of the calculations are previously published in Refs. \textsuperscript{13} and \textsuperscript{43}. The constrained volume relaxation was also performed with VASP\textsuperscript{44}, using the Atomic Simulation Environment Python package.\textsuperscript{45} The optimization of the scalar volume was performed in a gradient-free fashion through repeated one-shot, self-consistent DFT calculations, using the Brent method implemented in scipy. Volumes were bounded between 10 Å$^3$ (to prevent negative volumes) and two times a volume predicted with the data-mined lattice scheme (DLS) as implemented in Pymatgen.\textsuperscript{46} A rough initial volume guess (prior to DLS volume prediction) was generated with a linear model on composition trained on ICSD structures. Structures that ran into the upper bound volume during the bounded optimization tended to be unstable i.e., the energy continues to decrease as the volume increases, and were pruned from the database. Finally, we ensured the volume-energy curve was sufficiently smooth and removed structures where the minimum energy was more than 10 meV/atom lower than the second-lowest energy on the volume-energy curve.

#### 3.3.4 Data Quality Control

A number of data quality control checks were performed to remove problematic structures and relaxations from the DFT database prior to fitting the GNN model. First, we removed calculations derived from different ICSD prototypes that relax to the
same final structure upon full DFT relaxation. We observed that despite being given different initial prototypes, multiple relaxations for the same composition would occasionally converge to the same fully-relaxed structure. As this complicates the accurate splitting of train and validation structures, we removed duplicated results by comparing their fingerprints after relaxation (Section 3.4). We used scikit-learn to recursively cluster all fully-relaxed structures, using a cosine distance of 0.01 as the distance threshold and the maximum distance between clusters as the merging criterion. For each composition, only a single fully-relaxed structure per cluster was kept (one with the lowest energy), resulting in 13,133 fewer DFT data points. Next, we removed 1,391 unconstrained DFT relaxations where a lower energy was obtained from the constrained relaxation. These calculations indicated that the full DFT relaxation reached a local energy minimum.

We next removed crystals with energies and volumes well outside the expected range. We fit a robust linear model to predict total energy as a function of crystal composition using scikit-learn, and removed 1,551 calculations (10 full-relaxed, 1,541 volume-relaxed) with either a residual energy less than -2 eV/atom or greater than 5 eV/atom, or a residual volume less than -20 Å³/atom or greater than 50 Å³/atom. The final dataset sizes are as follows: 16,409 ICSD, 52,949 fully-relaxed, and 58,669 volume-relaxed structures.

### 3.4 Structure Fingerprints and Distances

Similarity between structures was calculated using the Matminer Python package. Fingerprints for each site were calculated using a local order parameter fingerprint, and converted to a crystal-level fingerprint by taking the mean and standard deviation over each site. Notably, the fingerprint method did not consider the overall volume of the unit cell, nor the chemical identity of the element at each site. Distances between crystal structures were then calculated using the cosine distance method as implemented in scikit-learn.

### 3.5 Surrogate Model Training

Of the ~128,000 training structures, we used stratified random sampling to hold out 1,500 structures for validation and 1,500 for testing. We also selected 100 compositions uniformly at random and held out their structures (1,492). We trained the model with a batch size of 64 structures for 100 epochs over the training data. To optimize training, we used the AdamW algorithm with an initial learning rate of $10^{-4}$, decayed by $\sim 10^{-5}$ each update step. We set the weight decay to an initial value of $10^{-3}$, also decayed by $\sim 10^{-5}$ each update step.

### Software and Data Availability

The code and data used to train the GNN models, the main results, and structures presented in this work are available at [github.com/jlaw9/upper-bound-energy-gnn](https://github.com/jlaw9/upper-bound-energy-gnn) (see also doi.org/10.5281/zenodo.7089031). Code used to run the RL optimization is available at [github.com/jlaw9/rl_materials](https://github.com/jlaw9/rl_materials).

### References

2306–2309.


39 Y. Dan, Y. Zhao, X. Li, S. Li, M. Hu and J. Hu, *npj Computational Materials*, 2020, 6, 84.


