

Accelerating materials discovery with Bayesian optimization and graph deep learning

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Machine learning (ML) models utilizing structure-based features provide an efficient means for accurate property predictions across diverse chemical spaces. However, obtaining equilibrium crystal structures typically requires expensive density functional theory (DFT) calculations, which limits ML-based exploration to either known crystals or a small number of hypothetical crystals. Here, we demonstrate that the application of Bayesian optimization with symmetry constraints using a graph deep learning energy model can be used to perform "DFT-free" relaxations of crystal structures. Using this approach to significantly improve the accuracy of ML-predicted formation energies and elastic moduli of hypothetical crystals, two novel ultra-incompressible hard MoWC₂ (P6₃/mmc) and ReWB (Pca2₁) were identified and successfully synthesized via *in situ* reactive spark plasma sintering from screening 399,960 transition metal borides and carbides. This work addresses a critical bottleneck to accurate property predictions for hypothetical materials, paving the way to ML-accelerated discovery of new materials with exceptional properties.

Keywords: Materials discovery; Bayesian optimization; Graph neural network; Deep learning

1. Introduction

The accurate prediction of novel stable crystals and their properties is a fundamental goal in computation-guided materials discovery. While *ab initio* approaches such as density functional theory (DFT) [1,2] have been phenomenally successful in this regard [3–6], their high computational cost and poor scalability have limited their broad application across vast chemical and structural spaces. As a result, high-throughput DFT screening has been mostly performed on ~ O(100 - 1000) crystals with relatively small unit cells.

To circumvent this limitation, machine learning (ML) has emerged as a new paradigm for developing efficient surrogate models for predicting materials properties at scale [7–12]. Such ML models are usually trained on large databases of materials

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properties [13-15] to learn the relationship between input chemical and/or structural features and target properties (e.g., formation energies, band gaps, elastic moduli, etc.). Only ML models utilizing structural as well as chemical features can distinguish between polymorphs and be universally applied in materials discovery across diverse crystal structures. In particular, graph neural networks, where atoms and bonds in crystals are represented as nodes and edges in a mathematical graph, have emerged as a particularly promising approach with state-of-theart accuracy in predicting a broad range of energetic, electronic and mechanical properties [16-23]. For instance, Bartel et al. [24] has recently shown that while composition-based ML models generally do not achieve sufficient accuracies in energies to predict stability, structure-based ML models such as crystal graph convolutional neural network (CGCNN) [18] can achieve the necessary accuracies for stability evaluations.

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Ironically, a critical bottleneck in the application of structurebased ML models for materials discovery is the requirement for equilibrium crystal structures as the inputs. These are obtained by "relaxing" initial input structures along their potential energy surfaces, which are typically computed via expensive DFT calculations. While there have been recent efforts [25,26] at deriving accurate interatomic forces from graph representations, the application has been limited to a few molecular systems or constrained chemical spaces.

Here, we propose a Bayesian Optimization With Symmetry Relaxation (BOWSR) algorithm to obtain equilibrium crystal structures for accurate ML property predictions without DFT. Utilizing a highly efficient MatErials Graph Network (MEGNet) formation energy model [16], we demonstrate that BOWSRrelaxed structures can serve as accurate inputs to ML property models, yielding far higher accuracy in the prediction of various materials properties. Finally, we demonstrate the power of this approach by screening ~400,000 transition metal borides and carbides for ultra-incompressible hard materials. Two new materials with relatively low predicted energies above hull [27] were successfully synthesized and demonstrated to have exceptional mechanical properties, in line with the ML prediction.

2. Results

2.1. Bayesian optimization with symmetry relaxation algorithm Bayesian optimization (BO) is an adaptive strategy for the global optimization of a function. In crystal structure relaxation, the function to be optimized is the potential energy surface, which expresses the energy of the crystal as a function of the lattice parameters and atomic coordinates. In the BOWSR algorithm, the symmetry (space group) of the lattice and the Wyckoff positions of the atoms are constrained during the relaxation process, i.e., only the independent lattice parameters and atomic coordinates are allowed to vary. The BO goal is then the minimization of the following mapping:

$$\mathbf{x} := \{a, b, c, \alpha, \beta, \gamma, \vec{c_1}, \vec{c_2}, \ldots\}$$

$$\tag{1}$$

$$x_{\rm opt} = \operatorname{argmin} U(x), U : \mathbb{R}^n \to \mathbb{R}$$
(2)

where $\{a, b, c, \alpha, \beta, \gamma\}$ and $\{c_1, c_2, \ldots\}$ represent the independent lattice parameters and the atomic positions for a *P*1 crystal, respectively, and *U*(.) is the energy of the system. The schematic of the BOWSR algorithm as well as two examples of the geometry parameterization for a high-symmetry cubic crystal and a lowsymmetry triclinic crystal are shown in Fig. 1.

The convergence accuracy and speed of the BOWSR algorithm are set by the energy evaluator U(.), which can be any computational model, including *ab initio* methods, empirical potentials, and surrogate ML models. In this work, we have elected to use a MEGNet formation energy model previously trained on the DFT-computed formation energies of 133,420 Materials Project crystals [13]. This MEGNet model has a cross-validated mean absolute error (MAE) of 26 meV atom⁻¹, which is among the best accuracy among general ML models thus far [22,18]. Comparisons between different energy evaluators are demonstrated in the next section. Examples of the convergence of the BOWSR algorithm using the MEGNet energy model are shown in Fig. S1.

2.2. Properties prediction

Elemental substitution is a common, chemically intuitive approach to deriving potential new compounds. For instance, the rock salt LiCl can be derived from rock salt NaCl by substituting Na for the chemically similar Li. Here, we demonstrate the potential for BOWSR to substantially enhance ML property predictions of the formation energies and elastic moduli (bulk and shear moduli) of substituted crystals. The dataset comprises a total of 12,277 and 1,672 unique crystals with pre-computed DFT formation energies and elastic moduli, respectively, from the Materials Project [13]. These crystals belong to 144 (35 binary, 91 ternary, and 18 quaternary) common structure prototypes in the Inorganic Crystal Structure Database (ICSD) [28,29]. Each prototype comprises at least 30 compositions (statistical distribution shown in Fig. S2). For each crystal in the dataset (e.g., rock salt GeTe), another crystal with the same prototype but a different composition (e.g., rock salt NaCl) was selected at random and elemental substitutions (Na-Ge, Cl-Te) were performed to arrive at an "unrelaxed" structure. The BOWSR algorithm was then applied to obtain a BOWSR-relaxed structure. It should be noted that relative to the unrelaxed crystals, the BOWSR-relaxed crystals have volumes that are much closer to the corresponding DFT-relaxed crystals, as shown in Fig. S3. The unrelaxed, BOWSR-relaxed, and the original DFT-relaxed structures were then used as inputs for property predictions using MEGNet models. These MEGNet models were trained on the DFT-computed formation energies and elastic moduli (bulk modulus K_{VRH} and shear modulus G_{VRH}) of 133,420 and 12,179 crystals, respectively, from the Materials Project.

Fig. 2 compares the MEGNet model predictions using the unrelaxed, BOWSR-relaxed, and DFT-relaxed structures as inputs with respect to DFT-computed values. The mean absolute errors (MAEs) of the MEGNet models using the DFTrelaxed structures provide a best-case performance baseline. It should be noted that the MEGNet models were trained using a superset of data from the Materials Project that includes the DFT-relaxed structures [13]. Hence, the reported MAEs of MEGNet predictions using DFT-relaxed structures in this work are much smaller than the previously reported MAEs of these MEGNet models from cross-validation and should not be considered as a metric for MEGNet performance. Using the unrelaxed structures as inputs results in much higher, positively skewed MAEs in the MEGNet formation energy prediction compared to using DFT-relaxed structures. This is because the unrelaxed structures have lattice parameters and atomic positions that can deviate substantially from the ground state DFT-relaxed structures, resulting in higher energies. Using the BOWSR-relaxed structures as inputs reduces the MAEs by a factor of four, from 363 meV atom⁻¹ to 88 meV atom⁻¹. The R^2 also substantially increases from 0.67 to 0.96, and the error distribution is Gaussian-like with a mean close to 0. Similarly, large improvements in the MEGNet predictions of the elastic moduli are also observed using the BOWSR-relaxed structures compared to using unrelaxed structures, with MAEs in the

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FIG. 1

Bayesian Optimization With Symmetry Relaxation (BOWSR) algorithm. **a**, The BOWSR algorithm parameterizes each crystal based on the independent lattice parameters and atomic coordinates based on its space group. The potential energy surface is then approximated by initializing a set of training observations and energies from the ML energy model. Bayesian optimization is then used to iteratively propose lower energy geometries based on prior observations. **b**, Two examples of the geometry parameterization for cubic perovskite SrTiO₃ and triclinic PdN₂C₁₂. For the high-symmetry cubic perovskite, the lattice parameter *a* is the only independent parameter, and all atoms are in special Wyckoff positions with no degrees of freedom in the fractional coordinates. For the triclinic crystal, all six lattice parameters and all atomic coordinates are independent parameters.

 $\log_{10} K_{\text{VRH}}$ and $\log_{10} G_{\text{VRH}}$ reducing by half. We tested the sensitivity of the BOWSR algorithm to the initial structures used to perform elemental substitution. Using four randomly chosen parent structures with different lattice parameters for each prototype, the above procedures were repeated and the results are shown in Fig. S4. The BOWSR-relaxed structures exhibit consistently low errors regardless of initial structure selection.

We tested the sensitivity of the BOWSR algorithm to the accuracy of the energy evaluator by artificially introducing Gaussian noise into the MEGNet formation energy prediction. The energy errors from the BOWSR-relaxed structures are linearly correlated with the errors of the surrogate ML model with the root mean square error (RMSE) ranging from 27 to 1000 meV atom⁻¹ (Fig. S5), which indicates the robustness of the BO propagation and the broad applicability of the BOWSR algorithm to any



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Performance of MEGNet materials properties predictions for three levels of relaxation. Three levels of relaxation are served as inputs for MEGNet materials properties predictions — unrelaxed, BOWSR-relaxed, and DFT-relaxed structures. **a**, **b**, and **c** show the parity plot of MEGNet prediction on formation energies, bulk moduli, and shear moduli, respectively. **d**, **e**, and **f** show the errors distribution on the corresponding materials property.

surrogate ML models. The same linear correlations are also observed between the elastic moduli errors and the errors of the surrogate ML model, as shown in Fig. S5c and S5d. We have also tested the effect of different energy evaluators with different accuracies, including DFT and a composition-based ML model (Magpie + XGBoost model [30,24,31]). As shown in Fig. S6, the DFT energy evaluator yields the lowest MAEs. In fact, the MAE in MEGNet-predicted formation energy for the DFT energy evaluator is comparable to that of the MEGNet formation energy model itself, providing further evidence that the BOWSR algorithm performs similarly to typical relaxation algorithms used in DFT calculations. The MAEs using the composition-based Magpie + XGBoost energy evaluator are the largest. In particular, the MAE in MEGNet-predicted formation energies is unacceptably large ($384 \text{ meV atom}^{-1}$), rendering it useless for stability predictions. The MEGNet energy evaluator yields MAEs that are much closer to using a DFT energy evaluator, and more crucially, the errors in MEGNet-predicted formation energies are centered around zero.

2.3. Discovery of ultra-incompressible hard materials

We used the BOWSR algorithm with the MEGNet models to rapidly screen hundreds of thousands of candidates for novel ultra-incompressible hard materials, as shown in Fig. 3. Given that binary compounds have already been extensively explored in the literature [32,33], we targeted our search in 12 ternary $M'_x M''_y X_z$ chemical spaces, where M', M" = Mo, W, Os, or Re and X = B or C. These elements were selected based on their common occurrences in ultra-incompressible hard binary compounds. By combinatorially applying elemental substitutions to 5,555 ternary structures prototypes in the ICSD [28,29], 399,960 candidates were generated and relaxed using the BOWSR algorithm with the MEGNet energy model. The

mechanical properties using MEGNet property models. The stability metric used was the energy above hull $E_{\rm hull}^{\rm MEGNet}$, which was computed using the predicted formation energy E_{f}^{MEGNet} with the 0 K phase diagram in the Materials Project database [27,13,34]. At this intermediate stage, a relatively generous threshold of $E_{\text{hull}}^{\text{MEGNet}} < 100 \text{ meV atom}^{-1}$ was used to obtain candidates that are likely to be thermodynamic stable [35]. Of these, candidates with relatively high MEGNet-predicted bulk and shear moduli ($K_{\text{VRH}}^{\text{MEGNet}} > 250$ GPa and $G_{\text{VRH}}^{\text{MEGNet}} > 100$ GPa) were identified. Similar to the stability criterion, the mechanical criteria used are slightly lower than the conventional threshold for ultra-incompressibility to account for the higher MAE of the MEGNet elastic moduli predictions [33]. DFT relaxations and energy calculations were then carried out on the 1,603 candidates that passed all three ML-based screening criteria. Subsequently, expensive DFT elastic tensor calculations [36] were performed on the 143 candidates that have DFT $E_{\text{hull}}^{\text{DFT}} < 100 \text{ meV} \text{ atom}^{-1}.$

BOWSR-relaxed candidates were then screened for stability and

Table 1 summarizes the computed elastic properties of the top ten candidates with the highest computed bulk modulus together with other well-known ultra-incompressible materials. Attempts were then made to synthesize all ten candidates with eight unique compositions via *in situ* reactive spark plasma sintering (SPS) using elemental precursors in the appropriate ratios (see Methods). Two crystals, $MoWC_2$ ($P6_3/mmc$) and ReWB ($Pca2_1$), were successfully synthesized and confirmed via X-ray diffraction (XRD, Fig. 4a) as single phase, while the synthesis of the other six compositions yielded multiple phases (see Figs. S7–S12). Henceforth, we will refer to the two novel phases of $MoWC_2$ ($P6_3/mmc$) and ReWB ($Pca2_1$) simply as $MoWC_2$ and ReWB, respectively.

FIG. 3

Flowchart of ultra-incompressible materials discovery leveraged by the BOWSR algorithm and MEGNet models. The materials candidates were generated by elemental substitution to structure prototypes. These candidates were relaxed by the BOWSR algorithm and subsequently screened by their predicted thermodynamic stability and mechanical properties. The screened candidates were further verified by DFT calculations, and the highranked candidates were directed to synthesis attempts. Quantity in the parenthesis shows the number of candidates at each stage.

The mechanical properties of MoWC₂ and ReWB were measured using the pulse-echo method [39,40]. As shown in Fig. 5a and b, the experimentally-measured bulk and shear moduli are in excellent agreement with both the MEGNet and DFT predictions. Both new materials exhibit ultra-incompressibility, with bulk modulus close to or larger than 300 GPa [33]. MoWC₂ also exhibits high estimated Vickers hardnesses H_v of 36.6 at 0.49 N indentation load and 20.9 GPa at 9.8 N load (Fig. 5c). ReWB has a comparatively lower measured hardness of 29.5 at 0.49 N load and 17.6 GPa at 9.8 N load. The H_v values at 0.49 N load are within 20–25% of those derived from the MEGNet and DFT predicted shear moduli via the empirical relation $H_v = 0.151G$ [38], as shown in Fig. 5d.

3. Discussion

Many materials properties, such as formation energies, mechanical properties, etc., exhibit a strong dependence on the crystal structure. However, obtaining equilibrium crystal structures as inputs to accurate ML models still requires expensive *ab initio* computations. By coupling an accurate MEGNet energy model with Bayesian optimization of symmetry-constrained parameters, we demonstrate that the new algorithm can reasonably approximate equilibrium structures. The resulting substantial improvements in ML property predictions enable the rapid screening of ~400,000 candidate crystals for stability and exceptional mechanical properties, 10^3-10^4 orders of magnitude larger than that accessible by high-throughput DFT calculations.

The effectiveness of the BOWSR algorithm is limited by the accuracy of the energy evaluator (Fig. S6). While the MEGNet formation energy model has been selected in this work, we foresee that the future development of more accurate ML energy models may improve the quality of the BOWSR-relaxed structures, and subsequent ML property predictions, even further. Here, the search for ultra-incompressible materials has been chosen as a model problem due to the high cost of acquisition of elastic moduli via standard DFT approaches, but the approach outlined can be readily extended to any property for which a reliable ML model can be developed. It should be noted, however, that there is an inverse relationship between the cost of acquisition and the training data size; hence, datasets on expensive properties (e.g., elastic moduli, optical properties, etc.) tend to be much smaller in size compared to cheaper properties, making it more difficult to build reliable ML models for high-cost properties. While approaches such as transfer learning or multi-fidelity models have been shown to mitigate this trade-off to some extent [16,17,41,42], the generally higher errors in ML models for high-cost properties should be factored into the screening process in the thresholds.

Finally, we note that an alternative approach is to obtain atomic forces and stresses by differentiating the energies with respect to atomic positions. We have tested this approach using the MEGNet energy model with the traditional Limited-memory Broyden-Fletcher-Goldfarb-Shanno (L-BFGS) optimization algorithm to relax structures. As can be seen from Table S2, the MAEs of the MEGNet predicted formation energies and elastic moduli are the highest for the L-BFGS approach. We believe that the MEGNet energy model are not sufficiently accurate to obtain reliable atomic forces via differentiation. Typically, models for accurate energies and forces, e.g., interatomic potentials, include well-converged forces in the training data.[43]. However, such training data is not readily available for the diverse structures and chemistries studied in this work. The key advantage of the BOWSR approach is that it requires energy evaluations only, and our work has in fact shown that it performs similarly to a direct relaxation approach. We have also validated the BOWSR approach using alternative ML property models based on CGCNN and found a similar twofold reduction in the MAEs in predicted energies and elastic moduli, as shown in Fig. S13.

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TABLE 1

DFT-computed bulk modulus (K_{VRH}), shear modulus (G_{VRH}), Young's modulus (E_{VRH}), Poisson's ratio (ν) and energy above hull (E_{hull}) for the top 10 candidates with regard to K_{VRH} in descending order. MoWC² and ReWB are bolded as they are successfully synthesized by experiments. Some of the known ultra-incompressible materials are used as references.

	$K_{ m VRH}$ (GPa)	$G_{ m VRH}$ (GPa)	$E_{ m VRH}$ (GPa)	v	$E_{ m hull}$ (meV atom ⁻¹)
Candidates					
ReOsB ($P\bar{6}m2$)	370.7	241.3	594.7	0.233	31.7
ReOsB_2 ($P6_3/mmc$)	367.3	220.9	552.0	0.250	87.8
$MoWC_2 (PG_3/mmc)$	357.9	260.5	628.8	0.207	96.3
ReWB (Fddd)	356.8	176.9	455.5	0.287	20.6
$\text{Re}_{13}\text{WB}_9$ ($P\bar{6}m2$)	353.1	177.0	455.1	0.285	88.4
ReWB (<i>Pca21</i>)	352.6	144.1	380.4	0.320	33.1
OsWB (Pbam)	351.1	183.1	467.9	0.278	43.3
ReWB (Cmce)	350.9	161.5	420.1	0.301	32.6
$Re_6W_7B_8$ (<i>P6/m</i>)	348.4	182.8	466.8	0.277	22.2
ReW_2B_2 (P4/mbm)	345.8	156.0	406.8	0.304	72.1
Known materials					
C (<i>Fd</i> 3 <i>m</i>)	430.3	503.6	1086.9	0.079	136.4
WC (<i>P</i> 6 <i>m</i> 2)	389.8	280.0	677.8	0.210	1.1
BN (F43m)	370.1	382.8	852.4	0.116	77.3
ReB_2 (P6 ₃ /mmc)	334.9	272.3	642.7	0.180	4.7

FIG. 4

Two new materials proposed by the BOWSR algorithm and MEGNet prediction confirmed by XRD characterizations. **a**, Measured and calculated XRD patterns of two materials (ReWB and MoWC₂). The major peaks are indexed for reference. The pymatgen library [37] was used to calculate the XRD patterns of the DFT-relaxed crystal structures. Minor shifts in peak positions between the measured and calculated XRD patterns can be attributed to the systematic errors between DFT and experimentally-measured lattice parameters. The comparison in lattice parameters between BOWSR-relaxed, DFT-relaxed, and experimental structures is shown in Table S1. **b**, Crystal structures and space group of these two materials. The predicted energy above hull for ReWB and MoWC₂ are 66 and 7 meV atom⁻¹, respectively.

FIG. 5

Experimental measurements and theoretical prediction of mechanical properties for the new materials. Comparisons of **a**, bulk moduli and **b**, shear moduli between MEGNet, DFT and pulse-echo measurements. **c**, Measured Vickers microhardness of ReWB and MoWC₂ under loads ranging from 0.49 N to 9.8 N. **d**, Comparisons between the hardness derived from MEGNet predicted bulk modulus and shear modulus [38] and the hardness measured by Vickers indentation at the low load (0.49 N). The DFT calculated results are referenced. The error bar represents the standard deviation of multiple experimental measurements.

4. Material and methods

4.1. Bayesian optimization with symmetry relaxation algorithm Geometry relaxation of a crystal structure requires the optimization of up to 3N + 6 variables – six lattice parameters and three fractional coordinates for each of the *N* atoms. By constraining the symmetry to remain unchanged during relaxation can reduce the number of independent variables considerably [44–46]. The open-source *spglib* [47] package was used for symmetry determination. The search for optimized symmetry-constrained lattice parameters and atomic coordinates that minimize the total energy was then carried out via Bayesian optimization inputs to reduce the tendency of the BO process being dominated by parameters with large magnitudes. This approach has been previously used for geometry optimization along the imaginary phonon modes [46].

Using a Latin hypercube sampling, a set of training observations $D \sim \{(x_i, U(x_i)) \ i = 1 : m\}$ were initialized, where the x_i are the *m* independent lattice parameters and atomic coordinates and U(.) is the energy of the corresponding structure evaluated by the surrogate model (see Eqs. (1) and (2)). The BO strategy comprises two steps [48]:

- 1. A Gaussian process (GP) model is trained on the initialized training observations D to approximate the U(x). The Rational Quadratic kernel [49] is adopted as the covariance function of GP. The noise level of GP model is set to the root mean square error (RMSE) of the energy model.
- 2. The acquisition function that balances the exploitation and exploration is calculated for samples in the search space apart from the training observations and the candidate with optimal acquisition function is proposed to be evaluated (formation energy prediction by surrogate ML model). Exploitation represents the samples with high predicted mean from the GP, and exploration accounts the samples with high predictive uncertainty [50–52]. Here, we chose the expected improvement as the acquisition function, which can be analytically expressed as [53,54]:

$$E[I(x)] = (\mu(x) - U(x^+) - \xi) \cdot \Phi(Z) + \sigma(x) \cdot \phi(Z)$$
(3)

and

$$x^{+} = \underset{i=1,\dots,n}{\operatorname{argmax}} U(x_{i}) \tag{4}$$

$$Z = \frac{\mu(x) - U(x^+) - \xi}{\sigma(x)} \tag{5}$$

where $\mu(x)$ and $\sigma(x)$ are the mean and standard deviation of the posterior distribution on *x* from the GP, respectively, and $\Phi(x)$ and $\phi(x)$ are the cumulative distribution function (CDF) and probability density function (PDF), respectively. The ξ parameter can be tuned to balance the trade-off between the first term (exploitation) and the second term (exploration) in Eq. (3). Until the maximum number of iteration steps is reached, the sample with optimal acquisition function was iteratively augmented to the training observations and used to update the GP surrogate model in the next loop.

It should be noted that by removing the symmetry constraint, i.e., treating all crystals as having triclinic *P*1 symmetry, the BOWSR-NoSymm yields much higher errors (see Fig. S14) than BOWSR. This can be attributed to the limitation of BO in optimizing the high dimensional parameter space that scales linearly with the number of atoms in crystals without symmetry. In this work, the number of initialized training observations and the maximum number of iterations were both set at 100 to achieve the best trade-off between accuracy and efficiency (see Fig. S14).

4.2. Materials graph network models

The Materials Graph Network (MEGNet) models used in this work are based on the same architecture as our previous work [16]. Briefly, three graph convolutional layers with [64, 64, 32] neurons were used in each update function, and the shifted softplus function was used as the non-linear activation function. A set2set readout function with two passes was used after the graph convolution steps. The cutoff radius for constructing the neighbor graph was 5 Å. The MEGNet formation energy (E_f) and elasticity (K_{VRH} and G_{VRH}) models were trained using the 2019.4.1 version of Materials Project database [13] containing 133,420 structure-formation energy and 12,179 structure-bulk/shear modulus data pairs. Each dataset was split into 80%:10%:10% train:validation:test ratios. During the model training, we used a batch size of 128 structures, and set the initial learning rate to 0.001 in the Adam optimizer. All models were trained for a maximum of 1500 epochs with an early stopping callback, which terminates the model training if the validation error does not reduce for 500 consecutive steps. The mean absolute errors (MAEs) of E_f , $\log_{10}(K_{\text{VRH}})$ and $\log_{10}(G_{\text{VRH}})$ models in test data are 26 meV atom $^{-1}$, 0.07, and 0.12, respectively.

4.3. Elemental substitution

The elemental substitution is performed by taking a crystal structure with known chemistry and substituting the elements with target elements within the structure. For example, an unrelaxed rock salt GeTe can be obtained from elemental substitution to the rock salt NaCl using Ge and Te as target elements. Unlike the ionic substitution in previous works[55,56], elemental substitution exhibits no constraint of charge neutrality and thus can be used for exploring hypothetical materials in a broader range, such as intermetallics and covalent systems.

4.4. DFT calculations

The DFT relaxations, energy and elastic tensor calculations for the small number of candidates that passed the ML screening were carried out using Vienna *ab initio* simulation package (VASP) [57] within the projector augmented wave approach [58]. The exchange–correlation interaction was described using the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) [59] functional for structural relaxations and energy calculations. The plane wave energy cutoff was set to 520 eV, and the k-point density of at least 1,000 per number of atoms was used. All structures were relaxed with energies and forces converged to 10^{-5} eV and 0.01 eV/Å, respectively, consistent with the calculation setting used in the Materials Project [13]. The elastic tensor calculations were performed using the procedure described in previous work [36]. A tighter energy convergence criterion of 10^{-7} eV was used, and strains with magnitude of (-1%, -0.5%, 0.5%, 1%) were applied to each of the 6 independent components of strain tensor.

4.5. Synthesis

Bulk specimens of candidates ReOsB, ReOsB2, MoWC2, ReWB, Re13WB9, OsWB, Re6W7B8, and ReW2B2 were synthesized via in situ reactive spark plasma sintering (SPS). Elemental powders of Mo, W (>99.5% purity, ~325 mesh, Alfa Aesar), Re (~99.99% purity, ~325 mesh, Strem Chemicals), Os (~99.8% purity, ~200 mesh, Alfa Aesar), boron (~99% purity, 1–2 μ m, US Research Nanomaterials), and graphite (~99.9% purity, 0.4-1.2 μ m, US Research Nanomaterials) were utilized as precursors. For each composition, stoichiometric amounts of elemental powders were weighted out in batches of 5 g. The powders were first mixed by a vortex mixer, and then high energy ball milled (HEBM) in a Spex 8000D mill (SpexCertPrep) by tungsten carbide lined stainless steel jars as well as 11.2 mm tungsten carbide milling media (ball-to-powder ratio ≈ 4.5 :1) for 50 min. 0.05 g or ~ 1 wt% of stearic acid was used as lubricant in the milling process. After HEMB, the as-milled powder mixtures were loaded into 10 mm graphite dies lined with graphite foils in batches of 2.5 g, and subsequently consolidated into dense pellets via SPS in vacuum ($< 10^{-2}$ Torr) by a Thermal Technologies 3000 series SPS machine. The HEBM and powder handing were conducted in an argon atmosphere (with O₂ level <10 ppm) to prevent oxidation.

During the SPS, specimens were initially heated to 1400 °C at a rate of 100 °C/min under constant pressure of 10 MPa. For the final densification, the temperature was subsequently raised at a constant rate of 30 °C/min to a final isothermal sintering temperature, which was set at different levels for different target compositions—1800 °C (ReWB), 1700 °C (MoWC2 and Re₆W₇B₈), 1600 °C (Re₁₃WB₉ and ReW₂B₂), or 1500 °C (ReOSB, ReOSB₂, and OsWB), and maintained isothermally for 10 min. Meanwhile, the pressure was increased to 50 MPa at a ramp rate of 5 MPa/min. The final densification temperature was optimized for each specimen to achieve a high relative density while prevent specimen melting due to overheating. The *in situ* reactions between elemental precursors likely took place during the initial temperature ramping. After sintering, the specimens were cooled down naturally inside the SPS machine (with power off).

4.6. Experimental characterization

Sintered specimens were first ground to remove the carboncontaminated surface layer from the graphite tooling, and polished for further characterizations. X-ray diffraction (XRD) experiments were conducted using a Rigaku Miniflex diffractometer with the Cu K α radiation at 30 kV and 15 mA. The Vickers microhardness tests were carried out on a LECO diamond microindentor with loading force varying from 0.49 N (50 gf) to 9.8 N (1 kgf) and constant holding time of 15 s, abiding by the ASTM Standard C1327. Over 20 measurements at different locations were conducted for each specimen at each indentation load to ensure statistical validity and minimize the microstructural and grain boundary effects. In particular, over 30 measurements were conducted for each specimen at 9.8 N indentation load.

The Young's and shear moduli of the specimens were calculated from the ultrasonic velocities measured with a Tektronix TDS 420A digital oscilloscope, following the ASTM standard A494–15. Multiple measurements were conducted at different locations.

Data availability

The BOWSR algorithm has been released as open source code in a Github repository at https://github.com/materialsvirtual-lab/maml/tree/master/maml/apps/bowsr.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This research was primarily supported by the National Science Foundation Materials Research Science and Engineering Center program through the UC Irvine Center for Complex and Active Materials (DMR-2011967). The authors also acknowledge the use of data and software resources from the Materials Project, funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division under contract No. DE-AC02-05-CH11231: Materials Project program KC23MP, and computing resources provided by the Extreme Science and Engineering Discovery Environment (XSEDE) under grant ACI-1548562.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, athttps://doi.org/10.1016/j.mattod.2021.08. 012.

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