

Stability and Equilibrium Structures of Unknown Ternary Metal **Oxides Explored by Machine-Learned Potentials**

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Cite This: J. Am. Chem. Soc. 2023, 145, 19378-19386 **Read Online** ACCESS III Metrics & More Article Recommendations Supporting Information Evolutionary algorithm ABSTRACT: Ternary metal oxides are crucial components in a Metal A wide range of applications and have been extensively cataloged in Energy experimental materials databases. However, there still exist cation SPINNER combinations with unknown stability and structures of their 11 compounds in oxide forms. In this study, we employ extensive മ 250 500 750 Ó 1000 crystal structure prediction methods, accelerated by machine-Metal Generation learned potentials, to investigate these untapped chemical spaces. We examine 181 ternary metal oxide systems, encompassing most Equilibrium structure cations except for partially filled 3d or f shells, and determine their Phase stability lowest-energy crystal structures with representative stoichiometry calculation derived from prevalent oxidation states or recommender systems.

phases, the majority of which incorporate noble metals. Comparisons with other theoretical databases highlight the strengths and limitations of informatics-based material searches. With a relatively modest computational resource requirement, we contend that heuristic-based structure searches, as demonstrated in this study, offer a promising approach for future materials discovery endeavors.

INTRODUCTION

Owing to large electronegativity, oxygen forms stable compounds with practically every metal atom. The ternary metal oxide, incorporating two species of metal atoms with distinct sizes and electronic shell structures, exhibits a variety of crystal structures and functionalities. Some well-known examples are BaTiO₃ for ferroelectrics,¹ BiVO₄ for water splitting,² BiFeO₃ for photovoltaics,³ LiCoO₂ for cathodes in Li-ion batteries,⁴ and LaAlO₃ and SrTiO₃ for high-k dielectrics.⁵ As such, ternary metal oxides constitute one of the most plentiful entries in materials databases, such as the Inorganic Crystal Structure Database (ICSD).⁶

Consequently, we discover 45 ternary oxide systems containing stable compounds against decomposition into binary or elemental

Despite the rich library, roughly one-third of all of the possible cation combinations of ternary metal oxides are yet to be cataloged in the experimental databases.⁷ This prompts the question of whether stable compounds exist within these uncataloged chemical spaces, and if they do, what their equilibrium structures are. The discovery of new ternary metal oxides through experiments alone is resource-intensive and time-consuming. Alternatively, theoretical databases such as the Materials Project (MP),8 Open Quantum Materials Database (OQMD),9 and Automatic-FLOW (AFLOW)¹⁰ provide hypothetical structures that are obtained by mainly exploiting known prototypes.^{11–19} For instance, Hautier et al. discovered hypothetical ternary oxides using the probabilistic prototype searching method.²⁰ However, such data-mining approaches cannot find ground states with prototypes outside the database.²¹ This challenge can be addressed by directly

searching equilibrium structures, a procedure called crystal structure prediction (CSP), in which heuristic approaches are employed to find the lowest-energy structure in the configuration space under a given composition.^{22,23} However, the effectiveness of this approach is limited due to the high computational cost of density-functional theory (DFT) calculations, and an exhaustive search of the structure space, which is often necessary for finding complicated equilibrium phases of ternary metal oxides, is not practically achievable.²⁴

Stable

Unstable

In recent years, there has been growing interest in machinelearned potentials (MLPs) as an alternative to the DFT method, given their ability to calculate the energy of structures several orders of magnitude faster than DFT, while maintaining similar accuracy.²⁵ In our previous work, we found that the MLPs trained with disordered phases (amorphous and liquid phases) have shown high fidelity as a surrogate model of DFT for the heuristic method of CSP.²⁶ Based on this idea, we developed a systematic CSP program called SPINNER (Structure Prediction of Inorganic crystals using Neural Network potentials with Evolutionary and Random searches),

Received: June 13, 2023 Published: August 11, 2023





utilizing MLPs within the evolutionary algorithm.²⁷ On the benchmark test on the experimental structure database, SPINNER identified ~80% ground-state structures among 60 ternary compounds with diverse crystal symmetries, doing so 10^2 to 10^3 times faster than DFT-based heuristic methods.

In this study, by harnessing the high speed and accuracy of SPINNER, we examine 181 ternary metal oxide systems, none of which have compositions registered in the experimental databases, encompassing most cations except for partially filled 3d or f shells, and determine their lowest-energy crystal structures with representative stoichiometry derived from prevalent oxidation states or recommender systems. Consequently, we discover 45 ternary oxide systems that contain stable compounds relative to elements or binary compounds, the majority of which incorporate noble metals. Comparisons with other theoretical databases highlight the strengths and limitations of informatics-based material searches.

METHODS

Training Machine-Learned Potentials. The training sets are generated by following mostly our previous study²⁷ except for slight modifications to reduce the computational cost. In detail, the initial MLP is trained over the melt-quench-annealing trajectory at the DFT level, which does not require any a priori information on the crystalline phase. The melt-quench-annealing simulation starts by premelting 60-70 atoms under the given composition at 4000 K over 4.5 ps. The simulation volume is adjusted such that the external pressure is close to zero. A temporary melting temperature (T_m) is then searched, and the liquid-phase simulation is conducted at T_m for 8 ps, followed by quenching to 300 K with a cooling rate of 200 K ps⁻¹. Finally, amorphous structures are sampled by annealing the system at 500 K for 4 ps. All DFT calculations are performed with the Vienna Ab initio Simulation Package (VASP)²⁸ using projector augmented-wave (PAW) pseudopotentials²⁹ and the Perdew-Burke-Ernzerhof (PBE) functional for exchange–correlation energy of electrons.³⁰ The cutoff energies for DFT molecular dynamics simulations are determined by the convergence test for premelted structures such that the energy, forces, and stress tensors converge to within 20 meV atom⁻¹, 0.3 eV Å⁻¹, and 10 kbar, respectively. A single k-point, either Γ or (1/4, 1/4, 1/4)³¹ is adopted for the Brillouinzone integration, and this choice is determined by the same convergence tests that determined the cutoff energies.

We adopt Behler-Parrinello-type neural network potentials (NNPs)³² with the symmetry function vectors as input features, as implemented in the SIMPLE-NN package.³³ For each pair of atomic species, 8 radial and 18 angular components are employed with cutoff radii of 6 and 4.5 Å, respectively. The NNPs are trained up to 500 epochs. The resulting root-mean-square errors (RMSE) of the validation set are 10 meV atom⁻¹, 0.5 eV Å⁻¹, and 20 kbar on average for the energy, force, and stress components, respectively. The 30-30 hidden layers are used in multilayer perceptrons. The input vectors are first decorrelated using principal component analysis (PCA) and then whitened to accelerate the learning speed.³⁴ The weight parameters of NNPs are updated utilizing a momentum-based Adam optimizer³⁵ with a batch size of 10. To prevent overfitting, an L2 regularization term is included in the loss function. 10% of the data is randomly selected for the validation set. To improve inference accuracy for ordered crystal structures, the NNPs are iteratively retrained with low-energy structures identified in the preliminary CSP as detailed in ref 27. In order to further estimate the errors against test structures that are not included in the training or validation set, we monitor the root-mean-square errors (RMSE) of structures generated through the evolutionary algorithm. The average RMSE value is 23 meV atom⁻¹, which is sufficiently small to be used in structure searching.

Evolutionary Algorithm. With the refined NNPs, we perform up to 1000 generations of the main CSP using the evolutionary algorithm using SPINNER.²⁷ The structures are generated through random

seeding, permutation, and lattice mutation in the ratios of 70, 20, and 10% respectively. The population of one generation is capped at 60. After the whole generation, the final candidate structures within the lowest 50 meV atom⁻¹ energy window are selected, and their DFT energies are calculated at the PBE level with full structural relaxations performed by an automated package, $AMP^{2,36}$ It is known that the error of the computed formation energy of oxides with respect to experimental data is lower using the strongly constrained and appropriately normed (SCAN) functional^{37,38} compared to the generalized gradient approximation (GGA) functional, though at the expense of 3–4 times increase in computational cost.^{39,40} Therefore, we identify the final ground state based on the SCAN we have confirmed that this energy evaluation scheme yields a reasonable accuracy when compared with the full relaxations using the SCAN functionals (see Figures S1 and S2).

Hull Energy Calculation. In order to determine the relative stability of the identified equilibrium structure compared to known binary and elemental phases, we evaluate the hull energies (E_{hull}) of the final candidates through full relaxations employing the SCAN functional. We employ the Pymatgen library to construct the ternary phase diagram using known binary and elemental phases and estimate the relative energy along the energy convex hull 4^{1-43} (see Figure 1a). We collect all experimental elemental and binary compounds from the MP database that can be derived from the target system and calculate their SCAN energies. For the accurate evaluation of total energies and the hull energy, we use PAW pseudopotentials that include semicore electrons as valence states. The cutoff energies and the k-point meshes are determined by the convergence test, ensuring that the energy values converge to within 2 meV atom⁻¹. We conduct structure optimizations until the force converges to within 0.02 eV Å⁻¹. The selection of stoichiometry as illustrated in Figure 1b will be explained in the next section.

RESULTS

Target Chemical Spaces. The target metal elements (A or B) in ternary metal oxide systems (A-B-O) are selected according to the following procedure: We first exclude partially filled 3d transition elements (V-Cu) because (i) the current generation of NNPs has not been fully tested on the subtle energies associated with diverse magnetisms in 3d metals^{44,45} and (ii) the relevant compounds are mostly identified in ICSD. (We validate that the complexity associated with diverse magnetisms is absent in 4d and 5d metals because of the small magnetic moments; see Figure S3 and the associated text for details.) Among the lanthanides (La-Yb), we only include La. Moreover, we omit semimetals (B, Si, Ge, As, Sb, Te, and Po) and radioactive elements (Tc and Po). This results in a set of 39 elements (Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, Sc, Y, La, Ti, Zr, Hf, Nb, Ta, Mo, W, Re, Ru, Os, Rh, Ir, Pd, Pt, Ag, Au, Zn, Cd, Hg, Al, Ga, In, Tl, Sn, Pb, and Bi), giving rise to 741 elemental combinations (see Figure 2). From these, we exclude chemical systems that contain any compositions already registered in experimental databases such as the Inorganic Crystal Structure Database (ICSD),⁶ International Centre for Diffraction Data (ICDD),⁴⁶ and Crystallography Open Database (COD).⁴⁷ (They are marked as gray tiles in Figure 2.) We also refer to FACT oxide (FToxid)⁴⁸ phase diagrams and exclude a system if the phase diagram precludes the existence of any ternary compounds in the corresponding space (see "X" marks in Figure 2). We omit Bi as all of the possible combinations already exist experimentally. As a result, we establish a total of 181 elemental combinations as the search space for this study, which are represented by nongray tiles in Figure 2. The number of target systems for each element is represented by pale-blue bars at the top. As



Figure 1. (a) Schematic representation of the hull energy evaluation. The energy convex hull of the ternary compositional space is constructed using SCAN energies of known binary and elemental phases. The hull energy is determined by calculating the energy difference between the lowest energy obtained from SPINNER and the energy of the convex hull surface for the corresponding composition. (b) Two approaches for selecting a representative composition is chosen based on the common oxidation state defined by the lowest formation energy of the binary oxides. It involves combining binary oxides with a common oxidation state in a 1:1 ratio. In the second method (right), if the highest-scoring composition suggested by the recommender system consists of cations in oxidation states different from the common oxidation state, it is also considered.

indicated by a rotated curly bracket at the top of Figure 2, many compounds include noble metals like Au, Ag, Pt, Pd, Rh, Ir, Os, and Ru (119 out of 181). This might be due to the high material costs and the weak tendency of these elements to form stable oxides. Many combinations including Be are also missing, partly due to the toxicity of Be.

In principle, the stability of A–B–O can only be definitely judged when all of the possible stoichiometries (i.e., ratios between elements) are examined. However, this is impractical since the current CSP is conducted within a specific compositional ratio. Therefore, we choose the representative composition ($A_x B_y O_z$) in two ways: by utilizing common oxidation states or by using a machine-learned recommender system⁴⁹ (see Figure 1b). First, we define the common oxidation states of a cation by considering well-established chemistry. If multiple oxidation states are possible, commonly occurring for many elements in this study, we select the oxidation state of the binary oxide with the lowest formation energy (per atom) under normal conditions, as calculated by the SCAN functional. The resulting oxidation states are compiled in Table 1. We then form a 1:1 addition of binary oxides for the representative composition. For example, in the case of Au-Nb-O, we combine Au₂O₃ and Nb₂O₅ from Table 1, resulting in the formula of AuNbO₄. We find that the 1:1 combination is the most frequent ratio (50%) among ternary oxides registered in ICSD, followed by 1:2 (18%) and 1:3 (11%). As for the second strategy, we use a machine-learned recommender in ref 49, which is based on the Tucker method that decomposes the ICSD data in tensor form into a core tensor and low-rank matrices.⁵⁰ We find that 76 out of the 181 systems possess the highest-rank compositions different from those selected by the first method. Among them, we select 49 cases in which the composition proposed by the recommender system suggests different oxidation states from the first method (for instance, $GaReO_4$ versus $GaReO_5$) because they represent opportunities for identifying compositions with stable compounds. Lastly, we perform CSPs with SPINNER for a total of 230 compositions in 181 systems.

Structure Prediction of Ternary Oxides. We use SPINNER for CSP of the given composition. In addition to stoichiometry, the formula unit (Z number) within the unit cell must also be specified when conducting CSP. Here, we adopt a Z number of 4, which is the most frequent among ternary oxides in ICSD (34%). Using this Z number, structures with Z = 1 and 2 can also be found. (The structures with Z = 1, 2, and 4 cover 63%.) For each A-B-O system, we obtain the structure with the lowest E_{hull} as compiled in Table S1 and colored in Figure 2. To note, we confirm that the phase separation is absent for every structure. A positive (negative) E_{hull} indicates that the structure is thermodynamically unstable (stable) against phase separation (see Figure 1a). We posit that a compound is synthesizable if $E_{\rm hull}$ is negative. Since we consider only one or two compositions, there is a possibility of false negatives (i.e., a compound is still synthesizable with other compositions in the same system). We also note that our definition of synthesizability does not take into account kinetic aspects and synthetic pathways. Although accounting for these factors would yield a more comprehensive analysis, it currently remains an ongoing challenge in the field of materials science.^{53,54} It is found that 45 systems contain 48 stable compounds with negative E_{hull} , where 20 compounds in 19 systems are highly stable ($E_{\text{hull}} < -50 \text{ meV atom}^{-1}$). Most of the newly discovered materials contain noble metals (35 systems), with Au being the most abundant (13 systems) (see the blue bars at the top of Figure 2). In Table S1, the compositions and E_{hull} values are compiled for the systems with $E_{\text{hull}} < 30 \text{ meV} \text{ atom}^{-1}$. In 18 cases, the oxidation state from the recommender system results in a lower E_{hull} than the common one (see the underlined compositions). The lowest-energy structures of some notable compounds are drawn in Figure 3. To check the dynamic stability of the stable compounds, we conduct density-functional perturbation theory calculations to obtain the dynamical matrices. We find that none exhibited significant imaginary frequencies (below 1 meV) at the Γ point (which means that they are dynamically stable), with the sole exception of Cs₂RhO₃. Cs₂RhO₃, however, displays an imaginary frequency of 36 meV. We then perturb the structure



Figure 2. Hull energy heatmap calculated for the selected elemental combinations. The elements are arranged in the order of increasing Mendeleev number, following ref 51. The map is partitioned to illustrate similar synthesis tendencies. The gray tiles on the map represent ternary oxides whose existence or nonexistence can be confirmed from the experimental databases. The colored tiles represent the hull energy values of the structures explored in this study, displayed on a color bar scale below the map. Systems with stable compounds are indicated by a green border. Tiles with black dots represent systems with stable compounds with structures that have no known prototypes. Tiles bordered by a dashed green box indicate systems where only OQMD^{9,52} registers a stable structure. The pale-blue bars above the heatmap indicate the number of target systems containing each element, while the blue bars represent the number of discovered systems with stable compounds.

Table 1. Selected Common Oxidation State (n) of Each Element (M)

| М | n | М | n | М | n | М | п |
|----|----|----|----|----|----|----|----|
| Li | +1 | Sc | +3 | Re | +7 | Zn | +2 |
| Na | +1 | Y | +3 | Ru | +4 | Cd | +2 |
| K | +1 | La | +3 | Rh | +3 | Hg | +2 |
| Rb | +1 | Ti | +4 | Pd | +2 | Al | +3 |
| Cs | +1 | Zr | +4 | Os | +4 | Ga | +3 |
| Be | +2 | Hf | +4 | Ir | +4 | In | +3 |
| Mg | +2 | Та | +5 | Pt | +4 | Sn | +4 |
| Ca | +2 | Nb | +5 | Ag | +1 | Tl | +3 |
| Sr | +2 | Mo | +4 | Au | +3 | РЬ | +2 |
| Ba | +2 | W | +6 | | | | |

by molecular dynamics simulations at 300 K and find that the relaxed structure is more stable than the original one by 13 meV atom⁻¹, without imaginary modes.

In Table S1, we provide the electronic properties of the identified stable structures that are obtained by using AMP². The band-gap is evaluated by one-shot hybrid functional calculation (HSE06),⁵⁵ and static dielectric constants are also calculated for materials with finite band gaps. The largest band

gaps, 6.3 and 5.4 eV, are found for the most stable compounds, Na_2HfO_3 and Cs_2HfO_3 , respectively (see Figure 3a,b). Their dielectric constants are 11.3 and 13.5, respectively, which are comparable to that of monoclinic HfO_2 (16.5).

In Figure 2, while 26 systems including Be are scanned, only 4 cases are found to be stable (Rb₂BeO₂, Cs₂BeO₂, Re₂BeO₈, and Au₂BeO₄). This is largely due to the high stability of BeO, which makes it challenging to transform a binary beryllium oxide into a ternary oxide. The small ionic radius of Be²⁺ (41 pm) also affects the stability of the ternary beryllium oxides, necessitating higher lattice energy when other metal atoms are introduced into the lattice sites between Be-O bonds. Also, the disparity in ion radii between Be and other metals leads to a lattice site mismatch, making it difficult to form stable ternary crystal structures. This is confirmed by search results showing that stable ternary beryllium oxides are discovered when combined with elements with smaller ionic radii, such as Al³⁺ (67.5 pm), but only metastable ternary beryllium oxides are discovered when combined with elements with larger ionic radii, such as Ga³⁺ (76 pm), Y³⁺ (104 pm), La³⁺ (117.2 pm), and Rh^{3+} (80.5 pm). Even Re_2BeO_8 (see Figure 3c), which we newly found, can form a stable phase because the ionic radius



Figure 3. Lowest-energy structures that are identified in this work are (a) Na_2HfO_3 , (b) Cs_2HfO_3 , (c) Re_2BeO_8 , (d) Y_2HgO_4 , (e) $NbAuO_4$, and (f) $YAuO_3$.

of Re⁷⁺ is small (52 pm). Among the stable ternary beryllium oxides, Rb₂BeO₂ and Cs₂BeO₂ can form stable phases due to inductive effects:⁵⁶ electropositive alkali metals can induce the oxidation of beryllium atoms by donating electron density to neighboring oxygen atoms, thereby increasing the ionization and lattice energies of ternary oxides.⁵⁷

Comparison with Computational Databases. Computational databases such as OQMD, AFLOW, and MP provide millions of theoretical structures, most of which are obtained through ion substitution into known compounds or prototypes. I^{1-19} In specific, the theoretical structures in the MP are primarily generated by data-mined ion substitution method,⁵⁸ and structures in the OQMD and AFLOW databases are largely predicted by a high-throughput structure generation method using specific types of prototypes.^{10,59} Such a datamining approach is highly efficient, but it risks overlooking materials with unknown prototypes. In contrast, the present direct approach is computationally more demanding but allows exploration of the structure space without any constraints. Thus, it would be worthwhile to compare these two contrasting methodologies. To this end, we have retrieved all of the theoretical structures belonging to the target A-B-O systems under study from the three databases, regardless of their stoichiometry. We then assessed their hull energies using the same reference structures (experimentally known unary and binary phases) and the method employed for calculating the hull energies of SPINNER structures. Out of 181 target combinations, 173, 86, and 181 systems include compositions that have at least one entry in the AFLOW, MP, and OQMD databases, respectively, leading to the retrieval of 368, 206, and 1674 structures from each database.

Figure 4a displays the number of systems found to be stable with a negative E_{hull} . Only one stable structure emerges from AFLOW as the energy distribution is primarily in the highenergy region (see Figure 4b). Structures from AFLOW are prevailed by the perovskite structure. The stability of the perovskite structure is typically evaluated based on Goldschmidt's tolerance factor and the octahedral factor.^{60,61} Our analysis reveals that 55 systems (out of a total of 181) concurrently meet these two conditions in ABO₃ stoichiometry. However, no perovskite structures from the AFLOW are identified to be stable, suggesting that other properties, such as electronegativity, also play a significant role.^{62–64} On the other hand, MP yields 11 systems with stable compounds. As illustrated in Figure 4b, the distribution near $E_{hull} = 0$ is higher for MP compared to other databases, which can be attributed to the use of a machine-learned crystal structure prediction scheme²⁰ and direct search.⁶⁵ Lastly, OQMD provides 29 systems with stable compounds, the highest count among the considered databases. This might be because OQMD generates structures from a substantially larger pool of prototypes than the other databases, as suggested by the highest number of retrieved structures (see above).

In Figure 4c, E_{hull}'s from AFLOW, MP, OQMD, and the present study are compared for the same system (numerical data are compiled in Table S1). Notably, several systems exist where OQMD predicts more stable phases than SPINNER such as below y = x in the third quadrant or the fourth quadrant (see the dashed line). We find that the oxidation states are different in most of these cases. For instance, in Pd-Mg-O, the present study identifies PdMgO₃ (-71.9 meV atom⁻¹) and PdMgO₂ (106.8 meV atom⁻¹) with Pd oxidation states of +4 and +2, respectively, while OQMD lists Pd_3MgO_6 $(-102.1 \text{ meV atom}^{-1})$, implying mixed Pd oxidation states of two +4 and one +2. When the present scheme is applied to Pd₃MgO₆, we find the structure identical to that in OQMD (see Table S2). Such untried stoichiometries were also suggested in the recommender system, but their priorities are distributed widely (from the 2nd to 19th ranks). This implies the need to scan a wide range of compositional ratios to identify correct equilibrium phases, particularly when the cation has multivalence states. It also indicates that the recommender system could be improved by utilizing theoretical structures, particularly for unexplored chemical spaces as in the present study.



Figure 4. Comparison of the search results with hypothetical structures in theoretical materials databases. (a) Number of systems with stable compounds identified in AFLOW, MP, OQMD, and the present study. (b) Distribution of hull energy (E_{hull}) for the most stable phases in each database, presented as normalized violin plots. The horizontal line at $E_{\text{hull}} = 0$ represents the stability criterion. (c) Comparison of hull energy between databases and the present study for the same system. Blue circles, yellow squares, and green triangles represent the hull energy of AFLOW, MP, and OQMD structures, respectively. Systems enclosed by a green dashed line indicate cases where OQMD predicts more stable phases than SPINNER. Symbols with a red outline indicate comparisons of the identical composition. The hull energies of structures from the AFLOW, MP, and OQMD are recalculated using the same reference structures (experimentally known unary and binary phases) and the method employed for calculating the hull energies of SPINNER structures.

When the composition is identical, SPINNER generally identifies a structure with lower energy compared to those in the databases, as indicated by the symbols with the red outline in Figure 4c. Specifically, among 35 cases in Table S1 with the same stoichiometry between OQMD and this work, our study yields lower energies for 22 systems, higher energies for 6 systems, and the same structure is found in 7 systems. On average, the energy is lower by 38.8 meV atom⁻¹ compared to those in OQMD. This suggests that the direct search typically outperforms the data-mining approach in the energy scale. Of the six cases where OQMD reports lower energies, three systems-RhIrO₄, RuOsO₄, and OsAlO₄-are speculated to form solid solutions in the rutile type, inferred from subtle energy variations of 1.2-16.4 meV atom⁻¹ among the candidate structures (Figure S4), which is smaller than the configurational entropy term at 300 K (18 meV). In these systems, OQMD and SPINNER show a slight difference only in the cation ordering. In the case of $RbRhO_2$, the NNP incorrectly predicts the energy of the structure in OQMD with a large error of 350 meV atom⁻¹, as its structural motif (Rb–O triangular prismatic polyhedron) is not present in the training set.

We use the AFLOW prototype library⁶⁶ to classify the prototypes of stable structures shown in Figure 2, and we find that 24 compounds out of the 48 stable compounds do not match any known prototypes (see dotted tiles). Interestingly, we find that AuYO₃, AuInO₃, and AuTIO₃ are in the same prototype, as do AuNbO4 and AuTaO4, which are not reported in the AFLOW library (see Figure S5). This means that the majority of the newly identified stable phases cannot be obtained through the data-mining approach.^{10,58,59} For example, in the composition of Y_2HgO_4 (see Figure 3d), the lowest-energy structure in the OQMD has an E_{hull} of -18.7 meV atom⁻¹. In contrast, SPINNER identifies a lower-energy structure with an E_{hull} of -26.0 meV atom⁻¹, which does not belong to any known prototype. These findings suggest that the direct search for equilibrium phases is essential for creating comprehensive materials databases for unexplored chemical spaces.

DISCUSSION

The previous section contrasts two approaches, direct versus data-mining^{10,58,59} in predicting crystal structures. The direct search outperforms the data-mining approach for a specific composition, indicating that the current library of prototypes is still insufficient. However, due to the high computational cost of structure search, the direct method, such as SPINNER, is not suitable for scanning diverse compositions, which is critical for multivalence cations. This is not an obstacle in the datamining approach in which simple ion exchange and structural relaxation can be done instantly. Thus, as seen above, the OQMD database could predict stable phases for some systems where SPINNER only produced unstable structures, by trying different oxidation states. This observation indicates a synergistic effect between direct and data-mining searches, suggesting that a complementary method would be desirable in materials discovery, striking a balance between exploration and exploitation. For instance, one can consider the crystal structure prediction method that primarily predicts using data-mining methods and strategically explores particular compositions with high levels of uncertainty to fine-tune the data-mining model on the fly. In addition, the data-mining method can assist in sampling training structures with diverse structural motifs that are not explicitly included in the training set generated by melt-quench simulations, which will increase the generalizability of the machine-learned potentials.

In the preceding section, we noticed a substantial difference among the databases. This is somewhat puzzling as all three databases are based on the data-mining approach. As the systems in the current study are less experimentally explored than other popular oxides, the selection of relevant prototypes might have varied among databases. As the specific algorithm for selecting prototypes is not openly available at this time, it is beyond the present work to clearly explain this discrepancy.

In this study, we limited the Z number to 4. When the resulting E_{hull} is slightly positive, one might consider trying higher Z numbers to identify stable phases. This can be done efficiently because the NNP is readily available, and the computational cost scales linearly with the number of atoms.⁶⁷ For instance, for Rb₂MgO₂ (0.1 meV atom⁻¹) and Sc₂HgO₄

(2.9 meV atom⁻¹), we performed CSP with Z = 8 and found a more stable structure for Sc₂HgO₄ (-5.9 meV atom⁻¹), while the structure for Rb₂MgO₂ remained the same. Likewise, one could try combinations other than 1:1 without changing the oxidation state where the trained NNP remains usable due to the transfer learning.²⁷ For example, for Rb₂MgO₂ (0.1 meV atom⁻¹), we perform CSP with the composition of Rb₆MgO₄ and found a stable structure with an E_{hull} of -6.3 meV atom⁻¹.

So far, the hull energies are evaluated by using reference structures that consists of experimentally reported binary and unary phases because the main objective of this study is to discover the chemical systems with synthesizable compounds that do not decompose into experimentally known phases. However, if one wants to identify truly synthesizable materials from the extensive pool of hypothetical structures, it is necessary to obtain the hull energies by including all theoretical structures from available databases. Indeed, among 48 stable compounds, we find that the hull energies of 8 materials (Na₂HfO₃, Cs₂HfO₃, Cs₂PdO₂, Cs₂PtO₃, Rb₂BeO₂, CsRhO₂, Au₂PbO₄, and PdMgO₃) change when including hypothetical structures from OQMD, AFLOW, and MP in the reference database, while the sign of hull energies remains negative. On the other hand, the hull energies of Rb₂PtO₃, PdHgO₃, LaAgO₂, RhIrO₄, RuOsO₄, OsAlO₄, Cs₂BeO₂, AgAuO₂, and RbRhO₂ increase to positive values, 23.3, 22.5, 30.2, 6.0, 3.3, 2.5, 1.5, 0.3, and 128.4 meV atom⁻¹, respectively, when evaluated by including theoretical structures. In Table S1, we also present E_{hull} values evaluated by including hypothetical structures.

In principle, our scheme is suitable for all types of materials, not limited to oxides, as it does not require prior knowledge of the target system. In our previous work,²⁷ we demonstrated the effectiveness of the present computational framework in identifying ground-state structures across diverse classes of materials such as sulfides, nitrides, and ternary metals. However, from a practical aspect, certain material groups such as halides and sulfides tend to exhibit a larger number of metastable structures during the evolutionary algorithm due to the rugged potential energy surface. In contrast, oxides generally have a smaller number of structures due to the limited types of polymorphs and structural orders resulting from their high bonding strength. Consequently, the computational cost for predicting crystal structures for materials such as halides and sulfides is typically higher than that for oxides. This is a practical issue, so we anticipate that further optimization of the computational parameters in our process will address this.

Regarding the computational cost, it takes about 60 h with a 32-core node to predict the structure for one composition on average, which includes the time for generating DFT training sets. This is 60% shorter than our previous work²⁷ owing to further optimization of the procedure for generating training sets, the most time-consuming step of the entire CSP process. Thus, on a medium-sized parallel computer, the complete scan of 181 systems took a couple of months. This represents a relatively modest requirement for computational resources, indicating that a heuristic-based direct search can be performed on a large scale, as demonstrated in the current work. We believe that this is a promising avenue for expanding the computational materials database in the future.

CONCLUSIONS

In summary, we examined hitherto unexplored ternary metal oxide systems using machine-learned potentials and the evolutionary structure searching algorithm. We identified 45 ternary oxide systems containing stable compounds that are resistant to decomposition into known experimental phases. Comparing our results with theoretical databases that mainly rely on data-mining methodologies for generating hypothetical structures, we discussed the strengths and weaknesses of both approaches and discussed the complementary methods to overcome such limitations. Considering the relatively moderate computational costs required for this work, our demonstration of heuristic-based direct structure searches offers a feasible and encouraging avenue in materials discovery.

ASSOCIATED CONTENT

Data Availability Statement

The main part of SPINNER is opened at https://github.com/ MDIL-SNU/SPINNER.²⁷ This program carries evolutionary structure searches using the trained NNP. SIMPLE-NN³³ for training NNPs is available at https://github.com/MDIL-SNU/ SIMPLE-NN_v2. All of the lowest-energy structures found by SPINNER are uploaded to SNUMAT⁶⁸ along with basic DFT results. SNUMAT supports RESTful API for search and download.

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.3c06210.

Validation of the methods, hull energy (E_{hull}) values, corresponding compositions, and calculated properties (PDF)

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Notes

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ACKNOWLEDGMENTS

This work was supported by Samsung Electronics Co., Ltd. (IO201214-08143-01) and the Creative Materials Discovery Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT (2017M3D1A1040689). A part of the computations was carried out at the Korea Institute of Science and Technology Information (KISTI) National Supercomputing Center (KSC-2022-CRE-0283).

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