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Krishna Chaitanya Pitike

Oak Ridge National Laboratory

Antonio Macias

University of California

Markus Eisenbach

Oak Ridge National Laboratory

Craig Bridges

Oak Ridge National Laboratory

Valentino Cooper (✉ coopervr@ornl.gov)

Oak Ridge National Laboratory <https://orcid.org/0000-0001-6714-4410>

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9 **Computationally accelerated discovery of high entropy pyrochlore oxides**

10 Krishna Chaitanya Pitike,¹ Antonio Macias,² Markus
11 Eisenbach,³ Craig A. Bridges,⁴ and Valentino R. Cooper^{1,*}

12 ¹*Materials Science and Technology Division,*
13 *Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*

14 ²*Department of Chemistry, University of California, Berkeley, CA 94720, USA*

15 ³*National Center for Computational Sciences,*
16 *Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*

17 ⁴*Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*

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Abstract

High entropy ceramics provide enhanced flexibility for tailoring a wide range of physical properties, emerging from the diverse chemical and configurational degrees of freedom. Expanding upon the endeavors of recently synthesized high entropy ceramics in rock salt, fluorite, spinel and perovskite structures, we explore the relative feasibility of formation of high entropy pyrochlore oxides, $A_2B_2O_7$, with multi-cation occupancy of the B -site, estimated from first principles based thermodynamic descriptors. Subsequently, we used Monte Carlo simulations to estimate the phase composition, oxygen vacancy concentration and local ionic segregation as a function of temperature and oxygen partial pressure. In parallel, we have investigated the synthesis of several multicomponent oxides with a pyrochlore composition, related to our computational investigations, resulting in several high purity pyrochlore oxides, in some cases with minor impurity phases. Ultimately, our approach allows us to evaluate potential impurity phases, ionic disorder and oxygen vacancy concentration in response to the experimental variables, thereby making realistic predictions that can direct and accelerate experimental synthesis of novel multicomponent ceramics.

I. INTRODUCTION

Since the discovery of an entropy stabilized oxide in 2015 [1], there has been a surge in the synthesis of new high entropy compounds (~ 25 compounds and counting) in ~ 10 structure types [2]. Yet there are more than 9000 structure types (see the Inorganic Crystal Structure Database (ICSD) Ref. [3]), that could still be potentially synthesized in the high entropy form. In this work, we have explored one such technologically important structure type — pyrochlore oxide, $A_2B_2O_7$.

Pyrochlore oxides can be generally formed with a large cation on the A -site (e.g., rare earth, alkali or an alkaline earth metal) and a smaller transition metal or post transition metal cation on the B -site. The flexibility in oxidation states and accommodating electronic interactions of the A - and B -site elements leads to rich functionality in the pyrochlore structure [4]. For example, pyrochlores and related structures have outstanding catalytic [5, 6], magnetic [7, 8] properties as well as exhibiting strong radiation and thermal resistance [9, 10]. These responses could be further tuned by modifying the structure to include multiple elemental species on the cation sublattices. For example, significant enhancement in multicomponent systems compared to the end members is demonstrated for oxygen conduction in disordered pyrochlores [11], piezoelectric properties in

* coopervr@ornl.gov

47 perovskites [12], and thermal resistance in high entropy ceramics [13, 14]. Furthermore, recent
48 investigations of ionic conductivity and mechanical properties of entropy stabilized oxide in the
49 rock salt structure revealed lithium superionic conductivity [15] and unusual elastic anisotropy [16],
50 respectively.

51 Thus far, the synthesis of a limited number of high entropy pyrochlores have been reported,
52 as obtained by heavy doping of lanthanides on the *A*-site [13, 17] and transition metals on the
53 *B*-site [18]. Specifically, our previous work on high entropy pyrochlores [18] has shown that
54 $\text{Nd}_2(\text{TaScSnHfZr})_2\text{O}_7$ and $\text{Nd}_2(\text{TiNbSnHfZr})_2\text{O}_7$ pyrochlore compositions are highly disordered
55 and phase pure. The grand challenge is however, a detailed predictive survey, to identifying new
56 candidates for high entropy pyrochlores obtained by combining multiple chemical species on the
57 target cation sites. In this work, we achieve this by computational exploration of the formation ability
58 of high entropy pyrochlores with 100 at.% La or 100 at.% Nd on the *A*-site and a combination
59 of transition metal cations on the *B*-site. Specifically, we utilize the enthalpy and entropy
60 descriptors — that we previously demonstrated [19] to accurately quantify the relative feasibility
61 of formation of high entropy single phase multi-component rock salt, *BO* oxides — to identify
62 five component combinations of *B*-site cations that are candidates for experimental synthesis.
63 We further extend this approach to include oxygen vacancy concentration in the high entropy
64 pyrochlore phase, as a function of temperature and oxygen partial pressure, thereby giving insights
65 for the experimental synthesis necessary for realizing single phase multicomponent compounds.
66 Employing this *predictive multiscale screening* approach would have multifold advantages over
67 conventional exploration via chemical synthesis. First, we can quickly filter the combinations that
68 are unlikely to form in a pure high entropy phase not only through chemical intuition, but also
69 by a rigorous thermodynamic assessment, derived from first principles calculations. Second, we
70 can predict the secondary phases and oxygen vacancy concentrations in the high entropy phase as
71 a function of temperature and oxygen partial pressure. Such predictions would serve as critical
72 feedback to a synthetic chemist for setting the experimental synthesis conditions.

73 Figure 1 presents the computational exploration methodology we have employed in this work.
74 At the first step, the cations are screened from all electropositive elements based on the preliminary
75 criterion (i) similar ionic radii for all species (ii) average nominal charge of the cation combination
76 should be consistent with the expected charge of the cation site. Values of the Shannon ionic radii
77 [20] and common oxidation states of the cations are useful for screening the cations at this step. In
78 the case of pyrochlores with La^{3+} or Nd^{3+} on the *A*-site, we consider the following 7 cations whose

FIG. 1. Predictive multiscale screening of high entropy compounds in a generic phase starting from readily available theoretical and experimental databases to screen potential elemental components. The multicomponent combinations are ranked by comparing *ab initio* computed enthalpy and entropy descriptors. Candidates for further experimental synthesis are predicted from Metropolis Monte Carlo simulations by comparing the temperature and oxygen partial pressure dependent phase fraction and disorder in finite length supercells.

combinations satisfy the chemical intuition, $B = \{\text{Hf}, \text{Nb}, \text{Sc}, \text{Sn}, \text{Ta}, \text{Ti}, \text{Zr}\}$, where 3+/5+ cations may be introduced together for charge balance, or where either 3+ or 5+ cations are introduced then oxygen deficiency/excess may be required. At the second step, the five component combinations are screened by estimating the enthalpy and entropy descriptors. Detailed description on estimation of these descriptors and their relationship to the configurational landscape are presented in our previous work [19]. The enthalpy and entropy descriptors are obtained from density functional theory (DFT) computed formation and mixing enthalpies — relative to the binary oxides, A_2O_3 and BO_2 — of the end member (one B -site cation) and two B -site cation compounds, respectively. At the third step, the selected five component compounds are evaluated for secondary phases and local ordering of cations through Metropolis Monte Carlo (MMC) simulations employing a nearest neighbor model (NNM). At this step, we can make accurate predictions of not only the phase fraction and local ordering, but also the oxygen vacancy concentration as a function of temperature and oxygen partial pressure. Based on the predictions at this step, promising candidates are chemically synthesized. The experimental validation of this theoretical predictions could serve as a critical feedback to improve the model. For example, unexpected secondary impurity phases can be added to the model thereby improving the accuracy of thermodynamics for the chemical composition, leading to more realistic predictions.

II. RESULTS

A. Structure and enthalpies of mixing

To assess the validity of the formation ability of the multicomponent high entropy compounds, we first consider the cation radii of all cations, whose combinations could potentially occupy the pyrochlore B -site, in combination with a 3+ cation, La or Nd on the A -site. Figure 2 presents the B -O bond length in the pyrochlore structure versus the sum of B -site and oxygen ionic radii ($R_B + R_O$) for the following cations — Ce^{4+} , Ge^{4+} , Hf^{4+} , Nb^{4+} , Nb^{5+} , Sc^{3+} , Sn^{4+} , Ta^{5+} , Ti^{3+} , Ti^{4+} , and Zr^{4+} . As expected, B -O bond lengths of these cations have strong linear correlation with their respective Shannon ionic radii. For our study the A - and B -sites in $A_2B_2O_7$ carry 3+ and 4+ nominal charges, respectively. We also consider Sc, Nb and Ta cations for B -site substitution, that have 3+, 5+ and 5+ nominal charges, respectively. In order to have an average charge of 4+ on the B -site in a five component pyrochlore, a combination of one 5+ and one 3+ cation is

FIG. 2. The sum of Shannon ionic radii of B -site cation and oxygen anion, $R_B + R_O$, plotted against the respective DFT computed B -O bond length for relevant cations.

required. For example, an equimolar combination of $\{\text{Hf}^{4+}, \text{Sn}^{4+}, \text{Zr}^{4+}, \text{Sc}^{3+}, \text{Ta}^{5+}\}$, would be charge balanced in a pyrochlore structure. Based on the B -site ionic radii and the charge balance, we reduce the possible B -site list to the following seven cations — Hf, Nb, Sc, Sn, Ta, Ti, and Zr. We have largely excluded cations with semi-filled d -states. A total of 21 five cation compositions can be generated using the seven potential cations ($7!/5!2! = 21$). Table I presents the 21 cation combinations each for La and Nd on the A -site along with their short form index. For the purpose of this study, we consider 100 at.% La or 100 at.% Nd on the A -site. For both La or Nd on the A -site, Hf^{4+} , Sn^{4+} and Zr^{4+} form pyrochlore ground state ternary structures. The remaining, Nb^{5+} , Ta^{5+} , Ti^{4+} , and Sc^{3+} form in the fergusonite, LaTaO_4 (NdTaO_4), perovskite-related layered orthorhombic (PRLO), and classical perovskite structures, respectively [21–33]. Experimentally observed ground state structures for every compound are tabulated in the Supporting Information.

An important aspect of predicting phase impurities is accounting for all the possible crystal structures that may compete with the pyrochlore structure. From the experimental literature and ICSD, we find that the one component $A_2B_2O_7$ and two component combinations $A_2(BB')_2O_7$ are likely to form in one of the six structure types — pyrochlore, fluorite, PRLO, LaTaO_4 (NdTaO_4), perovskite and fergusonite. Hence, in addition to the pyrochlore structure, we also include the aforementioned phases.

Figure 3 (a,c) depicts the $A_2B_2O_7$ pyrochlore, and (b,d) $A_2B_2O_8$ fluorite structures. Figures

FIG. 3. Eight formula unit representation of **(a)** $A_2B_2O_7$ pyrochlore and **(b)** $A_2B_2O_8$ fluorite structures. A smaller, two formula unit representations are shown for **(c)** pyrochlore and **(d)** fluorite structures. A-site and B-site cations are shown in green and blue spheres within the like colored translucent polyhedra, respectively. Oxygen ions are present at the corners of each polyhedron.

3(a,b) and (c,d) contain 16 and 4 B -sites, respectively. For both structures, the A - and B -site cations are ordered along the $\{110\}$, (face diagonal) directions. While the space group and positions of the A - and B -site cations are same for both structures, they differ in their oxygen environment, evident from the shapes of the polyhedra. For the fluorite structure, both cations have cubic coordinated oxygen environment. Whereas for the pyrochlore structure, the A - and B -site cations have hexagonal bipyramidal like and octahedral oxygen environments, respectively. The Wyckoff positions for both structures are given in the Supporting Information. Figures 3(c) and (d), shows a simpler representation with first nearest neighbor $B - B'$ interactions for pyrochlore and fluorite structures, respectively. Each B -site cation in both structures, is surrounded by six other B -site cations. For comparison, each cation in a rock salt structure is surrounded by 12 other cations. Structural models of the remaining structures are included in the Supporting Information.

Furthermore, for modeling purpose, we assume that the pyrochlore structure can undergo a phase transition to other structures by internal restructuring of the oxygen sublattice. Our model assumes free availability of oxygen ions — based on the oxygen partial pressure — wherever necessary when the composition is changed from $A_2B_2O_7$ to, for example, a $A_2B_2O_6$ perovskite or $A_2B_2O_8$ fluorite, etc. Specifically, the $A_2B_2O_8$ in fluorite or $NdTaO_4$ structure types can be obtained by oxidizing the $A_2B_2O_7$ pyrochlore structure with 1 oxygen ion per B -site. This assumption is justified because the pyrochlore to fluorite and PRLO structures is experimentally observed [34, 35].

In our previous study, exploring the formation ability of five component divalent cations in the

FIG. 4. Heat maps for mixing enthalpy in eV/B-site of $\text{La}_2(\text{BB}')_2\text{O}_n$ two component ternary oxides in phase P , $\Delta H_{\text{mix}}[A_2(\text{BB}')_2\text{O}_n, P]$, calculated from first principles using Eq. 1. Presented for (a) pyrochlore, (b) PRLO, (c) LaTaO_4 , (d) fluorite, (e) fergusonite and (f) perovskite phases. The annotation ‘G’ in each panel represents the *ground state* for the two cation combination. The color legend are shown separately for (a–c) and (d–f).

rock salt structure, we developed and discussed a set of thermodynamic descriptors based on the mixing enthalpies of two component oxides [19]. This approach allowed us to quickly screen the five component oxides directly from DFT calculations — without the high computational costs and configurational sampling, associated with large finite sized super cells. In the case of pyrochlores, the challenge associated with modeling large supercells is further exacerbated due to the larger number of atoms per unit cell, 11, compared to only 2 in the case of the binary oxides. Even though there are more atoms in the formula unit, they don’t increase the total configurational entropy. In fact the configurational entropy decreases due to the fact that disorder exists only for the six nearest neighbor B -site cations compared to the twelve nearest neighboring cations in the rock salt structure.

The mixing enthalpy, $\Delta H_{\text{mix}}[A_2(\text{BB}')_2\text{O}_n, P]$ of a two component oxide (TCO) $A_2(\text{BB}')_2\text{O}_n$,

in a generic phase, P , is estimated from DFT calculations as shown in Eq. (1).

$$\Delta H_{\text{mix}}[A_2(BB')_2O_n, P] = \frac{1}{2} \left\{ E_{\text{DFT}}[A_2(BB')_2O_n, P] - \left(\frac{2}{p}\right) E_{\text{DFT}}[A_pO_x, G] - \left(\frac{1}{q}\right) E_{\text{DFT}}[B_qO_y, G] - \left(\frac{1}{r}\right) E_{\text{DFT}}[B'_rO_z, G] - N_O \cdot \mu_O \right\} \quad (1)$$

$$N_O = n - \frac{2x}{p} - \frac{y}{q} - \frac{z}{r}$$

$E_{\text{DFT}}[A_pO_x, G]$, $E_{\text{DFT}}[B_qO_y, G]$ and $E_{\text{DFT}}[B'_rO_z, G]$ are the DFT total energies of the A_pO_x , B_qO_y and B'_rO_z oxides in their respective ground states, respectively. $E_{\text{DFT}}[A_2(BB')_2O_n, P]$ is the DFT total energy of the $A_2(BB')_2O_n$, TCO in phase P . n, x, y, z, p, q are integers representing the stoichiometric compositions of the oxide compounds. N_O and μ_O are the number of excess oxygens and oxygen chemical potential, respectively. Accounting for the experimental conditions of temperature and oxygen partial pressure:

$$\mu_O = \frac{1}{2} \left(\mu_{O_2}^0 + \Delta\mu_O \right) \quad (2)$$

$$\Delta\mu_O = \tilde{\mu}_{O_2}(p^0, T) + k_B T \ln \left(\frac{p_{O_2}}{p^0} \right)$$

$\mu_{O_2}^0$ is the oxygen chemical potential at ambient pressure p^0 and room temperature $T = T_{\text{RT}}$. $\tilde{\mu}_{O_2}(p^0, T)$ includes the contributions from rotations and vibrations of the oxygen molecule, as well as the ideal gas entropy at 1 atmosphere, tabulated in Refs. [36 and 37]. These are listed in thermodynamic JANAF tables and allow for the determination of the change in the oxygen chemical potential due to change in T [36]. p_{O_2}/p^0 is the oxygen partial pressure and k_B is the Boltzmann constant. The variation of $\Delta\mu_O$ as a function of p_{O_2} and T is presented in the Supporting Information. In the spirit of the nearest neighbor model [19, 38, 39], the value of $\Delta H_{\text{mix}}[A_2(BB')_2O_n, P]$, is used to describe the interaction energy between $B - B'$ cations in phase P , $\Delta H_{\text{mix}}^{B-B'} = \Delta H_{\text{mix}}[A_2(BB')_2O_n, P]$ in the five component oxide (FCO), as described in our previous work [19].

Figure 4 presents the mixing enthalpy heat maps for $\text{La}_2(BB')_2O_n$ calculated using Eq. (1) for the (a) pyrochlore, (b) PRLO, (c) LaTaO_4 , (d) fluorite, (e) fergusonite and (f) perovskite structures. The values in Figure 4 are plotted for $\Delta\mu_O = 0$. Similar heat maps for $\text{Nd}_2(BB')_2O_n$ are also given in the Supporting Information. There are 21 two component combinations and 7 one component pyrochlore compounds, obtained from 7 B -site cations. Out of these 28 compounds for both $A = \text{La}$ and Nd , we find that 10 compounds are stable as pyrochlore, 6 as PRLO, 8 as LaTaO_4 (NdTaO_4),

3 as fergusonite, and 1 as the perovskite structures. The values of the mixing enthalpies of these one and two component combinations in their ground states, are much smaller than the mixing enthalpies of the AO type binary oxides as shown in Figure 2 of Ref. [19], indicating that — in this case — the structures with two cation sublattices are thermodynamically more stable than the structures with only one cation sublattice. This is due to the large contribution of the lattice enthalpy generated from the ordering of the A – and B –site cations in the ternary oxide super lattice. We utilize the values of these mixing enthalpies as parameters in the nearest neighbor model to estimate the thermodynamic descriptors by systematically exploring local configurations as discussed in our previous work on high entropy oxides in rock salt structure [19].

TABLE I. The compositions and short form indices of five component combinations considered in this work.

Index	Composition	Index	Composition
La-1	$\text{La}_2(\text{HfNbScSnTa})_2\text{O}_7$	Nd-1	$\text{Nd}_2(\text{HfNbScSnTa})_2\text{O}_7$
La-2	$\text{La}_2(\text{HfNbScSnTi})_2\text{O}_7$	Nd-2	$\text{Nd}_2(\text{HfNbScSnTi})_2\text{O}_7$
La-3	$\text{La}_2(\text{HfNbScSnZr})_2\text{O}_7$	Nd-3	$\text{Nd}_2(\text{HfNbScSnZr})_2\text{O}_7$
La-4	$\text{La}_2(\text{HfNbScTaTi})_2\text{O}_7$	Nd-4	$\text{Nd}_2(\text{HfNbScTaTi})_2\text{O}_7$
La-5	$\text{La}_2(\text{HfNbScTaZr})_2\text{O}_7$	Nd-5	$\text{Nd}_2(\text{HfNbScTaZr})_2\text{O}_7$
La-6	$\text{La}_2(\text{HfNbScTiZr})_2\text{O}_7$	Nd-6	$\text{Nd}_2(\text{HfNbScTiZr})_2\text{O}_7$
La-7	$\text{La}_2(\text{HfNbSnTaTi})_2\text{O}_7$	Nd-7	$\text{Nd}_2(\text{HfNbSnTaTi})_2\text{O}_7$
La-8	$\text{La}_2(\text{HfNbSnTaZr})_2\text{O}_7$	Nd-8	$\text{Nd}_2(\text{HfNbSnTaZr})_2\text{O}_7$
La-9	$\text{La}_2(\text{HfNbSnTiZr})_2\text{O}_7$	Nd-9	$\text{Nd}_2(\text{HfNbSnTiZr})_2\text{O}_7$
La-10	$\text{La}_2(\text{HfNbTaTiZr})_2\text{O}_7$	Nd-10	$\text{Nd}_2(\text{HfNbTaTiZr})_2\text{O}_7$
La-11	$\text{La}_2(\text{HfScSnTaTi})_2\text{O}_7$	Nd-11	$\text{Nd}_2(\text{HfScSnTaTi})_2\text{O}_7$
La-12	$\text{La}_2(\text{HfScSnTaZr})_2\text{O}_7$	Nd-12	$\text{Nd}_2(\text{HfScSnTaZr})_2\text{O}_7$
La-13	$\text{La}_2(\text{HfScSnTiZr})_2\text{O}_7$	Nd-13	$\text{Nd}_2(\text{HfScSnTiZr})_2\text{O}_7$
La-14	$\text{La}_2(\text{HfScTaTiZr})_2\text{O}_7$	Nd-14	$\text{Nd}_2(\text{HfScTaTiZr})_2\text{O}_7$
La-15	$\text{La}_2(\text{HfSnTaTiZr})_2\text{O}_7$	Nd-15	$\text{Nd}_2(\text{HfSnTaTiZr})_2\text{O}_7$
La-16	$\text{La}_2(\text{NbScSnTaTi})_2\text{O}_7$	Nd-16	$\text{Nd}_2(\text{NbScSnTaTi})_2\text{O}_7$
La-17	$\text{La}_2(\text{NbScSnTaZr})_2\text{O}_7$	Nd-17	$\text{Nd}_2(\text{NbScSnTaZr})_2\text{O}_7$
La-18	$\text{La}_2(\text{NbScSnTiZr})_2\text{O}_7$	Nd-18	$\text{Nd}_2(\text{NbScSnTiZr})_2\text{O}_7$
La-19	$\text{La}_2(\text{NbScTaTiZr})_2\text{O}_7$	Nd-19	$\text{Nd}_2(\text{NbScTaTiZr})_2\text{O}_7$
La-20	$\text{La}_2(\text{NbSnTaTiZr})_2\text{O}_7$	Nd-20	$\text{Nd}_2(\text{NbSnTaTiZr})_2\text{O}_7$
La-21	$\text{La}_2(\text{ScSnTaTiZr})_2\text{O}_7$	Nd-21	$\text{Nd}_2(\text{ScSnTaTiZr})_2\text{O}_7$

B. Enthalpy and entropy descriptors from mixing enthalpies

In our previous work on predicting high entropy oxides in the rock salt structure [19], we have demonstrated that the enthalpy and entropy descriptors, m and σ , respectively, influence the

FIG. 5. A comparison of the enthalpy and entropy descriptors, m and σ , for all 21 five component (a) $\text{La}_2\text{B}_2\text{O}_7$ and (b) $\text{Nd}_2\text{B}_2\text{O}_7$ pyrochlores. Enthalpy and entropy descriptor differences between pyrochlore and PRLO structures, Δm and $\Delta\sigma$, for (c) $\text{La}_2\text{B}_2\text{O}_7$ and (d) $\text{Nd}_2\text{B}_2\text{O}_7$ compositions. Each data point is annotated with its index.

191 formation ability of a multi-component, single phase structure [40]. The expressions for calculating

the values of m and σ are given in Eq. 3.

$$m = \langle \Delta H_{\text{local}} \rangle \quad (3a)$$

$$\sigma = \sqrt{\langle \Delta H_{\text{local}}^2 \rangle - \langle \Delta H_{\text{local}} \rangle^2} \quad (3b)$$

$$\langle \Delta H_{\text{local}} \rangle = \frac{1}{N_{\text{local}}} \sum_{i=1}^{N_{\text{local}}} \left(\Delta H_i [\text{FCO}, P_i] \right) \quad (3c)$$

$$\langle \Delta H_{\text{local}}^2 \rangle = \frac{1}{N_{\text{local}}} \sum_{i=1}^{N_{\text{local}}} \left(\Delta H_i [\text{FCO}, P_i] \right)^2 \quad (3d)$$

$$\Delta H_i [\text{FCO}, P_i] = \frac{1}{n} \sum_{j=1}^n \Delta H_{\text{mix}} [B^i - B^j, P_i] \quad (3e)$$

where, $\langle \Delta H_{\text{local}} \rangle$ and $\langle \Delta H_{\text{local}}^2 \rangle$ are the mean values of the local mixing enthalpies and squared local mixing enthalpies, respectively. $\Delta H_{\text{mix}} [B^i - B^j, P_i]$ is the average mixing enthalpy of site- i with cation B^i , surrounded by cations, B^j . Essentially, the descriptors for the enthalpy and entropy, are obtained from exploring the local mixing enthalpies, $\langle \Delta H_{\text{local}} \rangle$, of all local configurations within the five component oxide (FCO). There are *six* first nearest neighbor B -site cations, surrounding each B -site cation in the pyrochlore structure. A local atomic configuration at a lattice site, i , constitutes chemical species occupied by the lattice site, B^i , along with the six nearest neighboring B -site cation species, B^j , $j = \{1, 2, 3, 4, 5, 6\}$. Blue atoms and their bonding environment in Fig. 3(c) represents the local configuration of a B -site.

In our previous work, we discuss the significance of exploring the energy landscape of the local configurations. When the distribution of local configurations is relatively narrow, indicating a small value for σ . Consequently, the entropy contribution ($-T\Delta S$) to the free energy of the high entropy structure (which is inversely proportional to the entropy descriptor, σ) would be large and negative. Furthermore, a small value for the enthalpy descriptor, contributes a small value to the free energy. Hence, an FCO with relatively low values for σ and m , should have a relatively high propensity for the formation of phase pure high entropy structure.

Figure 5 (a, b) plots the enthalpy vs entropy descriptors for all FCOs considered in this work with (a) La and (b) Nd on the A -site. Each data point represents a FCO and the closer it is to (0,0) the higher is its propensity to form a high entropy phase. The index of each FCO combination is annotated in the data point symbol. We find that the FCOs automatically fall into three clusters.

The cluster at top right corner of Figures 5 (a) and (b), with high- m and high- σ have low propensity to form in a high entropy pyrochlore phase. Each composition in this cluster contain both

215 Nb^{5+} and Ta^{5+} — is comprised of five component combinations with indices 1, 4, 5, 7, 8, 10, 16, 17,
 216 19, and 20. Such compositions with two parts 5+ cations, Nb and Ta, and one [or zero] parts Sc^{3+}
 217 cation, would have a charge balanced chemical composition of $A_2(\text{Nb}^{5+}\text{Ta}^{5+}\text{Sc}^{3+}BB')_2\text{O}_{7.2}$ [or
 218 $A_2(\text{Nb}^{5+}\text{Ta}^{5+}BB'B'')_2\text{O}_{7.4}$], inconsistent with the chemical composition of a pyrochlore structure
 219 type. Where, B , B' and B'' exclusively represent cations with 4+ oxidation state, such as Hf, Sn,
 220 Ti and Zr. For this cluster, both chemical intuition and our thermodynamic descriptors agree that
 221 the cation combinations without charge balance should have a low propensity to form in a high
 222 entropy pyrochlore phase.

223 The second cluster at the center of Figures 5 (a, b), with medium- m and medium- σ , is comprised
 224 of FCO combinations that have only one 5+ cation, Nb or Ta. The cluster contains 10 FCO
 225 combinations with indices 2, 3, 6, 9, 11, 12, 14, 15, 18, and 21. The charge balance for 8 of
 226 these combinations is obtained due to the presence of Sc^{3+} cation. While the charge balance
 227 in other 2 FCO combinations that do not contain Sc^{3+} (indices 9 and 15), may be achieved due
 228 to the presence of Ti, that could take on a 3+ oxidation state, this is not expected to occur in
 229 our high temperature reactions in air. We note that Ti in the 3+ oxidation state can be obtained
 230 under sufficiently reducing conditions; for example, Ti in the 3+ oxidation state in Ti_2O_3 oxide
 231 can be prepared by reducing TiO_2 with titanium metal at 1300 K [41]. All these five component
 232 combinations are charge balanced and could have medium propensity to form in the high entropy
 233 pyrochlore form.

234 The third cluster contains only one FCO, index 13, with $B = (\text{Hf}, \text{Sc}, \text{Sn}, \text{Ti}, \text{Zr})$. Even though
 235 according to the charge balance, the composition of this compound is $A_2(\text{Hf}^{4+}, \text{Sc}^{3+}, \text{Sn}^{4+}, \text{Ti}^{4+},$
 236 $\text{Zr}^{4+})_2\text{O}_{6.8}$ — i.e., 0.2 deficit of oxygen atoms per formula unit, for a pyrochlore structure, will later
 237 show that by accommodating oxygen vacancies, it is possible to obtain a phase pure pyrochlore
 238 structure with this composition. For further investigation, we have selected 11 FCO combinations
 239 from second and third clusters.

240 Furthermore, according to the mixing enthalpies of two component oxides [see Figure 4 (a) and
 241 (b)], we find that the PRLO structure competes with the pyrochlore structure. Other structures —
 242 fergusonite, $\text{LaTaO}_4/\text{NdTaO}_4$, perovskite and fluorite phases do not compete with the pyrochlore
 243 phase. Here, we compare the phase stability of the pyrochlore phase with the PRLO phase. Figures
 244 5 (c, d) plots the enthalpy and entropy descriptor differences, $\Delta m = m_{\text{pyrochlore}} - m_{\text{PRLO}}$ vs
 245 $\Delta \sigma = \sigma_{\text{pyrochlore}} - \sigma_{\text{PRLO}}$, respectively, for FCOs in the pyrochlore and PRLO structures. In other
 246 words, for combinations which are close to the $\Delta m = 0$ line and $\Delta m \geq 0$, the PRLO phase

competes with the pyrochlore phase. Hence these combinations may have low propensity to form in phase pure high entropy pyrochlore. We find that the values of the enthalpy and entropy descriptors of PRLO structures with indices La-2 (Nd-2), La-6 (Nd-6), La-9, La-11 (Nd-11), La-14 (Nd-14), La-15, La-18 (Nd-18), and La-21 (Nd-21), are comparable with the pyrochlore structure. As such these compounds could be competing for two high entropy phases and we expect them to form multiphase complex microstructures. After comparing the FCOs utilizing the enthalpy and entropy descriptors for the pyrochlore and competing PRLO structures, we down selected the following FCO combinations with indices La-3 (Nd-3), La-9 (Nd-9), La-12 (Nd-12), La-13 (Nd-13) and La-15 (Nd-15) for further evaluation. In the next section we describe our thermodynamic predictions for the high entropy phase as a function of experimental conditions, such as temperature, T and oxygen partial pressure p_{O_2}/p^0 .

C. Estimating experimental variables through Metropolis Monte Carlo simulations

We have ranked the relative tendency of formation of a high entropy pyrochlore phase from the enthalpy and entropy descriptors. This is the first step in choosing the five component combinations most probable to form high entropy compounds — i.e., low mixing enthalpies and low configurational entropies. In this section, we evaluate the variation of the phase composition and cation segregation, as a function of experimentally controllable variables, T and p_{O_2}/p^0 for the previously screened five component combinations. Evaluating T and p_{O_2}/p^0 dependence is a crucial step for determining the fraction of secondary phases, oxygen vacancy concentration and cation disorder that might emerge in the high entropy pyrochlore phase. We utilized the Metropolis Monte Carlo framework developed in our previous work [19] and extend the approach to include the thermodynamic contributions from oxygen partial pressure.

In addition to sampling configurations, we also sample phase composition by updating the global phase after each trial configuration obtained by atomic swapping. A detailed description of the Monte Carlo method, and scheme to sample atomic configurations and phase composition is given in Section IV B. Briefly, the total energy of the system depends not only on the mixing enthalpies but also on the oxygen chemical potential, μ_{O} as shown in the following equation,

$$\Delta H_{\text{total}}[\text{FCO}, P] = \sum_{i=1}^N \Delta H_i[\text{FCO}, P_i] + N_{\text{O}} \cdot \mu_{\text{O}} \quad (4)$$

where, N_{O} is the deficit oxygen present in the composition and $\Delta H_i[\text{FCO}, P_i]$ is the local mixing

enthalpy of B -site cation at site i (see Eq. 3e). μ_{O_2} further depends on T and p_{O_2}/p^0 as given in Eq. 2. The significance of the influence of oxygen chemical potential is emphasized below. For example, the presence of Sc^{3+} cations on a B^{4+} site could potentially induce oxygen vacancies adjacent to Sc^{3+} in the pyrochlore structure. The vacancy formation enthalpy was estimated in the pyrochlore structure for all two component combinations. Concurring with chemical intuition and charge balance, we find that the oxygen vacancy formation enthalpies are negative for two component combinations containing Sc. The oxygen formation enthalpies, $\Delta H_{\text{vac}}^{\text{O}}[B - B']$ are computed according to the following equation:

$$\Delta H_{\text{vac}}^{\text{O}}[B - B'] = E_{\text{DFT}}[A_2(BB')_2\text{O}_7] - E_{\text{DFT}}[A_2(BB')_2\text{O}_6] - \frac{1}{2} \cdot \mu_{\text{O}_2}^0 \quad (5)$$

In order to estimate the oxygen vacancy concentration of a five component pyrochlore, we consider the oxygen vacancy structures as a new phase ‘pyrochlore with vacancies’. A phase update is also performed in addition to the B -site cation swap. Below, we discuss the trends in expectation values of the phase fraction and short range order parameter as a function of T and p_{O_2}/p^0 , for the $\text{La}_2(\text{HfNbScSnZr})_2\text{O}_7$ composition. The results for other structures are presented in the Supporting Information and the summary is tabulated in Table II.

Figure 6 presents the expectation value of the phase fraction, $\langle \phi(P) \rangle$ as a function of T and p_{O_2}/p^0 for $\text{La}_2(\text{HfNbScSnZr})_2\text{O}_7$ in the (a) pyrochlore, (b) oxygen vacancies in the pyrochlore, (c) PRLO and (d) fergusonite structures. Other secondary phases such as fluorite and perovskite, have negligible phase fractions for this compound. At $T > 1800$ K and ambient oxygen partial pressure, the value of $\langle \phi(\text{pyrochlore}) \rangle > 96\%$. For practical purposes, we consider that the transition to phase pure pyrochlore occurs at $\langle \phi(\text{pyrochlore}) \rangle > 96\%$. Such an assumption is justified as discussed in our previous observations of the entropy stabilized rock salt oxide, where the secondary phases were not visible in the predicted X-ray powder diffraction pattern at this phase fraction secondary phases [1, 19].

Besides the transition to a pure pyrochlore phase at $T > 1800$ K, we also find that the oxygen vacancy concentration is $\sim 1.2\%$ in the pyrochlore phase. The vacancies are correlated with Sc^{3+} cation locations with no neighboring Nb^{5+} or Ta^{5+} . Furthermore, the transition temperature T_t decreases with p_{O_2}/p^0 . However, the oxygen vacancy concentration in the pyrochlore increases by decreasing p_{O_2}/p^0 . Similar phase diagrams for the other five component combinations, that are screened at the second step are given in the Supporting Information.

Figure 7 depicts the expectation value of the short range order parameter (SOP), $\langle \alpha_{BB'} \rangle$ as a func-

FIG. 6. Heat map of phase fraction, $\langle \phi(P) \rangle$ for $\text{La}_2(\text{HfNbScSnZr})_2\text{O}_7$ is plotted as a function of $\log(p_{\text{O}_2}/p^0)$ and T . (a) pyrochlore, (b) percentage vacancies in pyrochlore structure, (c) PRLO and (d) LaTaO_4 phases. The contour lines along with their annotated values are also given for each panel.

tion of T and p_{O_2}/p^0 for (a) Hf-Nb, (b) Sc-Sc, (c) Nb-Nb and (d) Nb-Sc in $\text{La}_2(\text{HfNbScSnZr})_2\text{O}_7$. Plots for SOPs of all combinations of cations are given in the Supporting Information. In our framework we do not consider the activation barrier for cation diffusion. Nevertheless, we find that the cation mixing happens at low temperatures $T < 500$ K. While, in reality the mixing of the cations typically occur at $T > 1000$ K for the ternary structures (for instance see Ref. [42]), we anticipate that the qualitative trends in the SOP should be unchanged. In general, we find that 4+ cations, Hf, Sn and Zr, mix easily at low temperatures in the pyrochlore phase. Whereas Nb^{5+} segregates to a fergusonite phase, as shown in Figure 6(d). In addition, Nb partially mixes with Sc in the pyrochlore phase (and also in the competing PRLO phase).

Table II summarizes the phase transitions temperatures (denoted by a pyrochlore phase fraction

FIG. 7. Heat map of short range order parameter for selected two component combination for $\text{La}_2(\text{HfNbScSnZr})_2\text{O}_7$ is plotted in separate panel as a function of $\log(p_{O_2}/p^0)$ and T . The contour lines along with their annotated values are also given for each panel.

of $\geq 96\%$) and other critical properties for the considered structural phases. Overall, we find that T_t for $A = \text{Nd}$ are smaller than their $A = \text{La}$ counterparts. These computational predictions were experimentally validated by attempting to synthesize the following compositions: $\text{La}_2(\text{NbScHfSnZr})_2\text{O}_7$, $\text{La}_2(\text{TaScHfSnZr})_2\text{O}_7$, $\text{La}_2(\text{NbTiHfSnZr})_2\text{O}_7$, $\text{La}_2(\text{ScTiHfSnZr})_2\text{O}_7$, $\text{La}_2(\text{CeTiHfSnZr})_2\text{O}_7$, and the Nd analogues of these compositions.

Figure 8 presents the powder X-ray diffraction pattern for five component B -site cation combinations mentioned in each panel with either (a) La and (b) Nd on the A -site. Even though our theoretical predictions generally agree with the experimental findings, there are a few noticeable discrepancies. First, due to the competing thermodynamics between the PRLO and pyrochlore phases, the former was predicted to persist as a secondary phase up to the transition temperature

TABLE II. Summary of the finite temperature properties, such as transition temperature, T_t , expectation value of oxygen vacancy concentration, $\langle\phi(\text{O}_{\text{vac}})\rangle$ for the $\text{La}_2\text{B}_2\text{O}_7$ and $\text{Nd}_2\text{B}_2\text{O}_7$ compounds obtained from Metropolis Monte Carlo simulations. In addition, we have also compared the predicted secondary phases with the experimentally observed secondary phases for each compound, where possible.

	Index	La-3	La-12	La-13	La-9	La-15
T_t [K]	$\log(p_{\text{O}_2}/p^0) = -30$	1400	1600	1600	1300	1400
	$\log(p_{\text{O}_2}/p^0) = 0$	2000	2100	1100	1900	2100
	$\log(p_{\text{O}_2}/p^0) = 5$	2200	2200	1100	2200	2300
$\langle\phi(\text{O}_{\text{vac}})\rangle$ [%]	$\log(p_{\text{O}_2}/p^0) = -30$	0.37882	0.37091	0.44835	0	0
	$\log(p_{\text{O}_2}/p^0) = 0$	0.26367	0.24961	0.34044	0	0
	$\log(p_{\text{O}_2}/p^0) = 5$	0.22144	0.23816	0.30370	0	0
Experimental Synthesis		Yes	Yes	Yes	Yes	No
Predicted Secondary Phases		PRLO & Fergusonite	PRLO & LaTaO ₄	PRLO & Perovskite	PRLO & Fergusonite	PRLO & LaTaO ₄
Experimental Secondary Phases		Negligible	PRLO	Perovskite	Pyrochlore	Not Available
Cation segregation		Nb-Nb & Nb-Sc	Ta-Ta & Sc-Ta	Sc-Sc & Ti-Ti	Nb-Nb & Ti-Ti	Ta-Ta
Supporting Information Figure		S4(a-d) & S9(a)	S6(a-d) & S11(a)	S7(a-d) & S12(a)	S5(a-d) & S10(a)	S8(a-d) & S13(a)
	Index	Nd-3	Nd-12	Nd-13	Nd-9	Nd-15
T_t [K]	$\log(p_{\text{O}_2}/p^0) = -30$	1300	1100	1100	1200	1200
	$\log(p_{\text{O}_2}/p^0) = 0$	1800	1800	1000	1800	1800
	$\log(p_{\text{O}_2}/p^0) = 5$	1900	1900	1000	2000	2000
$\langle\phi(\text{O}_{\text{vac}})\rangle$ [%]	$\log(p_{\text{O}_2}/p^0) = -30$	0.39469	0.38794	0.48623	0	0
	$\log(p_{\text{O}_2}/p^0) = 0$	0.26470	0.25746	0.34031	0	0
	$\log(p_{\text{O}_2}/p^0) = 5$	0.23732	0.24383	0.31862	0	0
Experimental Synthesis		Yes	Yes	Yes	Yes	No
Predicted Secondary Phases		PRLO & Fergusonite	PRLO & NdTaO ₄	PRLO & Perovskite	PRLO & Fergusonite	PRLO & NdTaO ₄
Experimental Secondary Phases		Fergusonite	None	Perovskite	None	Not Available
Cation segregation		Nb-Nb & Nb-Sc	Ta-Ta & Sc-Ta	Sc-Sc & Ti-Ti	Nb-Nb & Ti-Ti	Ta-Ta
Supporting Information Figure		S4(e-h) & S9(b)	S6(e-h) & S11(b)	S7(e-h) & S12(b)	S5(e-h) & S10(b)	S8(e-h) & S13(b)

FIG. 8. Experimental powder X-ray diffraction pattern for (a) La based five component sample and (b) Nd based five component oxide.

for all considered five component combinations. However the PRLO phase was only found as a minor impurity phase in the $\text{La}_2(\text{HfNbSnTiZr})_2\text{O}_7$ composition through powder X-ray diffraction. We believe that the PRLO phase can be easily transformed into the pyrochlore phase at high temperature, due to the close mixing enthalpy values. Furthermore, since the phase fraction of the pyrochlore is significantly greater in the sample than the PRLO structure, the surrounding pyrochlore structure propagates into the PRLO structure. This effect can be thought of similar to the substrate induced phases — where the substrate phase propagates into the thin film [43]. Second, we find the presence of the compound $A_2(\text{HfScSnTiZr})_2\text{O}_{7-x}$, where $A = \{\text{La}, \text{Nd}\}$, can be formed in the pyrochlore phase at $T \sim 1100$. However the oxygen vacancy concentration is expected to be quite large $\sim 2.5\%$, due to charge balance with Sc^{3+} on the B -site. Interestingly, the vacancy concentration can be decreased to $\sim 1.6\%$ by setting $T \sim 2400$ K and $p_{\text{O}_2}/p^0 \sim 10^5$. Whereas the powder X-ray diffraction for the same compound suggests that the samples are contaminated with secondary AScO_3 perovskite phases. The data indicate that the LaScO_3 and

338 NdScO_3 compounds are sufficiently stable that they would prefer to form under the synthesis
 339 conditions. Of the remaining compositions, most formed pure or nearly single phase products,
 340 with the exception of $\text{La}_2(\text{HfScSnTaZr})_2\text{O}_7$ which contains a significant secondary phase, that may
 341 be fluorite structured. Examination of the pattern suggests that two similar phases are present,
 342 perhaps due to poor diffusion, some compositional inhomogeneity remains that was difficult to
 343 remove during this solid state route. We note that it is challenging for powder X-ray diffraction
 344 data to distinguish between the changes in oxygen sublattice between pyrochlore and fluorite
 345 structure. Furthermore, for this compound the presence of the strong X-ray scatterers Hf^{4+} and
 346 Ta^{5+} on the B -site means that the difference in scattering power between the A - and B -site
 347 cations is relatively small, making the superstructure peaks from the cation sublattice ordering more
 348 difficult to observe when comparing the fluorite and pyrochlore structures. Therefore, based upon
 349 the computationally-derived expectation values of the phase fraction and cation segregation, we
 350 interpret the peak broadening in this case may be due to the local segregation of Ta along with Sc,
 351 leading to a minority pyrochlore phase with local variations in the lattice constant.

352 Finally, we would like to mention that we have not attempted to synthesize La-15 or Nd-15,
 353 even though we have computationally evaluated these compounds to have medium propensity
 354 to form in a high entropy phase. The experimental validation of La-15 and Nd-15 is yet to
 355 be explored. Furthermore, we did not consider Ce in our computational evaluation — of its
 356 ability to mix with other cations to form a high entropy pyrochlore due to its large Shannon radii
 357 compared with other radii. Nevertheless, we have attempted to synthesize $\text{La}_2(\text{CeHfSnTiZr})_2\text{O}_7$
 358 and $\text{Nd}_2(\text{CeHfSnTiZr})_2\text{O}_7$, as a test case for Ce based high entropy pyrochlores. Ce appears to
 359 drive the formation of secondary phases rather than form a single phase pyrochlore with 20 at.%
 360 Ce present on the B -site, despite the entropic driving force at the 1800 K synthesis temperature.
 361 Which is consistent with the chemical intuition as a rational for screening criterion.

362 III. DISCUSSION

363 We have utilized a generic framework — that we developed and extensively tested in our
 364 previous work on AO multicomponent oxides [19] — to screen high-entropy pyrochlores with
 365 five components on the B -site. We examined the potential secondary phases as a function of
 366 the experimentally controllable variables, temperature and oxygen partial pressure. The mean
 367 m and standard deviation σ , of the local mixing enthalpies calculated using the nearest neighbor

model, represent enthalpy and entropy descriptors of the five component combinations. Within this framework a five component combination with low values of m and σ — representing low mixing enthalpy and high configurational entropy — would have the highest propensity to form a high entropy pyrochlore phase. Here we reject the five component combinations that also have low value of m and σ in a different phase indicating the presence of thermodynamically competing phase. In this case, we rejected several five component combinations that have a PRLO phase competing with the pyrochlore phase. Starting from 42 five component combinations, 21 each with 100 at.% La and 100 at.% Nd on A -site, we were able to find 3 and 5 potential candidates with La and Nd on the A -site, respectively.

We have extended the Metropolis Monte Carlo framework to evaluate the influence of temperature and oxygen partial pressure on the tendency for phase segregation and to form secondary phases. More importantly, this approach now allows us to examine phase compositions, oxygen vacancy concentrations and short range order parameters as a function of experimentally controllable variables. For the pyrochlores, we find that the phase transition temperatures for $A = \text{Nd}$ are lower than their $A = \text{La}$ counterparts, indicating that pyrochlores with $A = \text{Nd}$ are easier to form. The presence of Sc induces oxygen vacancy concentration of $< 0.5\%$ at ambient oxygen partial pressure and $T = T_t$, which further decreases by increasing oxygen partial pressure. Furthermore, a combination of 3+ and 5+ cations tend to promote local segregation of pyrochlore phase, which decreases with increasing temperature. In this regard, the x-ray diffraction peak broadening for $\text{La}_2(\text{TaScHfSnZr})_2\text{O}_7$, as shown in second panel from top of Fig. 8, could be due to local segregation of Ta and Sc cations leading to local changes in lattices.

Out of the three compositions with $A = \text{La}$ that were predicted to have high propensity to form high entropy pyrochlore structure, $\text{La}_2(\text{HfNbScSnZr})_2\text{O}_7$ was experimentally synthesized as a pure high entropy pyrochlore structure. The remaining two compositions, $\text{La}_2(\text{HfScSnTaZr})_2\text{O}_7$ has local segregation of Ta-Sc cations and $\text{La}_2(\text{HfNbSnTiZr})_2\text{O}_7$ forms secondary perovskite related layered orthorhombic phases. Out of the five compositions with $A = \text{Nd}$ that were predicted to have a high propensity to form high entropy pyrochlore structures, $\text{Nd}_2(\text{HfScSnTaZr})_2\text{O}_7$ was experimentally synthesized as a pure high entropy pyrochlore structure. $\text{Nd}_2(\text{HfNbSnTiZr})_2\text{O}_7$ was synthesized with minor fergusonite secondary phases, agreeing with our previous neutron scattering analysis of this compound [18]. However the other two compositions $\text{Nd}_2(\text{HfNbScSnZr})_2\text{O}_7$ and $\text{Nd}_2(\text{HfScSnTiZr})_2\text{O}_7$ were observed to have fergusonite and perovskite secondary phases, respectively. We note that the predicted secondary phases for all structures agree with the experimental

400 observation.

401 While the utility of thermodynamic descriptors demonstrated in this work to predict the forma-
402 tion ability of high entropy pyrochlores are conceptually-simple and computationally-cheap, these
403 descriptors are robust enough to accommodate simple AO oxides to complex $A_2B_2O_7$ pyrochlores.
404 This work significantly advances the predictive capabilities that include the oxygen partial pres-
405 sure as an independent variable to predict impurity phases, local disorder and oxygen vacancy
406 concentrations. Furthermore, this framework is simple and flexible enough to accommodate other
407 independent variables such as the influence of mechanical strain on the phase stability of epitaxial
408 high entropy functional oxides — thereby predicatively screen the high entropy ceramics for target
409 properties. While the present effort is primarily focused on predicting new high entropy pyrochlores
410 and their experimental synthesis recommendations, other structures of interest can be systematically
411 identified using a similar multiscale screening approach.

412 IV. COMPUTATIONAL METHODS

413 A. Details of first-principles calculations

414 All DFT calculations were carried out using the plane-wave-based Vienna *ab initio* simulation
415 package VASP version 5.4.4, software package [44, 45] within the generalized gradient approxi-
416 mation (GGA) using the Perdew, Burke, and Ernzerhof for solids (PBEsol) exchange-correlation
417 functional [46]. The energy cutoff for the plane-wave basis set was 800 eV, and projected aug-
418 mented wave (PAW) potentials [47, 48] were used. VASP PAW potential files used in this study
419 and their valance electronic configuration are tabulated in the Supporting Information. A $6 \times 6 \times 6$
420 k -point mesh was utilized for sampling the Brillouin zone for a 22 atom unit cell and scaled
421 inversely with the number of atoms present in the unit cell. The bulk geometry was optimized with
422 a force convergence criterion of 1 meV/Å and the individual components of the stress tensor were
423 converged to ≤ 0.1 kBar.

424 Spin-unpolarized calculations were employed for estimating the mixing enthalpies. According
425 to experimental observations, pyrochlores with $A = \text{Nd}$ are antiferromagnetic (AFM) on the
426 A -site with all-in-all-out (AIAO) AFM ordering. However, it was recently reported that for the
427 case of structural thermodynamics, non-magnetic calculations would yield enthalpy values with
428 reasonable accuracy [49]. Hence, even in the case of Nd^{3+} containing compounds, we employed

only non-magnetic calculations.

B. Metropolis Monte Carlo Simulations

We employed Metropolis Monte Carlo simulations to study the mixing behaviour between different chemical species within the FCO at relevant temperatures ranging from $T = 300$ to 2400 K with a temperature step of $\Delta T = 100$ K. Atomic configurations — generated through randomly swapping unlike atoms between different lattice sites in a $3 \times 3 \times 15$ periodic supercell (containing 2160 B -site cations) — are sampled according to the Metropolis criterion. A trial configuration is accepted according to the Boltzmann probability, p_B

$$p_B = \text{Minimum} \left\{ \exp\left(\frac{-\Delta H}{k_B T}\right), 1 \right\} \quad (6)$$

where, $\Delta H = \Delta H_n^{\text{total}} - \Delta H_{n-1}^{\text{total}}$ is the change in total mixing enthalpy between n and $n - 1$ steps, caused by swapping unlike chemical species. k_B is the Boltzmann constant and T is the absolute temperature. The trial configuration is always accepted if $\Delta H \leq 0$. However, if $\Delta H > 0$ the trial configuration is accepted by chance according to the Boltzmann probability, p_B .

In addition to the sampling of atomic configurations, we also sample the phase composition through phase updates similar to the technique discussed in Ref. [19]. A ‘global’ phase P from one of the following phases — ground, pyrochlore, fergusonite, LaTaO_4 (NdTaO_4), PRLO, perovskite — is assigned to the atomic configurations. The ground state phase represents a mixture of multiple phases, where the fraction of each phase is obtained by counting the fraction of lattice sites of each phase. A phase update is done after each atomic swap according to the metropolis criterion. For example, a phase update from $P = \text{Ground}$ to $P = \text{Pyrochlore}$ is preferred according to the Boltzmann probability, p_B , where,

$$\Delta H = \Delta H_n^{\text{total}}[\text{FCO}, \text{Ground}] - \Delta H_{n-1}^{\text{total}}[\text{FCO}, \text{Pyrochlore}] \quad (7)$$

is the energy difference between the configuration in pure pyrochlore phase and the ground state phase with mixed phase composition. The expectation values of phase fraction $\langle \phi(P) \rangle$ and local short-range order $\langle \alpha_{B-B'} \rangle$, are determined at constant temperature.

The phase composition of each microstate is achieved by assigning a local ground-state phase, G_i , to each lattice site i as

$$\Delta H_i[\text{FCO}, G_i] = \text{Minimum}(\Delta H_i[\text{FCO}, P_i]) \quad (8)$$

It is crucial to note that the ground-state phase, G , of a microstate is a combination of all local phases. For example, at lattice site i , a chemical species B_i is assigned a local phase G_i — which is determined based on the minimum of the mixing enthalpies of all considered phases. The phase fraction, $\Phi(P)$, of a phase P is evaluated by dividing the number of occurrences of local phase P_i by the total number of lattice sites.

$$\Phi(P) = \frac{1}{N} \sum_{i=0}^N \delta(G_i, P) \quad (9)$$

where $\delta(G_i, P)$ is a Dirac delta function, which returns 1 if the local ground-state phase at lattice site i , $G_i = P$.

The value of the short range order parameter $\alpha_{BB'}$ of a microstate is estimated by averaging the number of atoms of species B' surrounding all atoms of species B . By the commutative relation, $\alpha_{BB'} = \alpha_{B'B}$, there are only 15 unique short-range order parameters in a five-component high-entropy compound.

V. EXPERIMENTAL METHODS

Rare-earth oxides (La_2O_3 , Nd_2O_3) and B -site metal oxides (ZrO_2 , HfO_2 , SnO_2 , TiO_2 , Ta_2O_5 , Nb_2O_5 , Sc_2O_3) were ground together in stoichiometric quantities. La_2O_3 , Nd_2O_3 and Sc_2O_3 were heated before weighing to 1000°C to decompose impurities (e.g., carbonate, hydroxide). Typically 1-2 g of starting material were ground in a mortar and pestle, then milled in a SPEX mill for several hours with YSZ balls. The collected powder was pressed into pellets and heated to 1500°C in air for 10 hours. The difference between quenching the samples in ice water versus slow cooling ($5^\circ\text{C}/\text{min}$ to room temperature) was investigated, and did not appear to influence the sample purity according to laboratory X-ray diffraction results. X-ray diffraction data were collected on a Panalytical Empyrian X-ray diffractometer using Cu K_α radiation.

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DATA AVAILABILITY

Raw data associated with all figures is available on request from the corresponding authors, V.R.C. (vrcooper@ornl.gov), or C.A.B. (bridgesca@ornl.gov).

AUTHOR CONTRIBUTIONS

K.C.P. performed first principles calculations, co-developed the theoretical framework, developed all computational codes including Monte Carlo code, performed Monte Carlo simulations, interpreted the computational results and wrote the manuscript with significant input from all other authors. M.E. co-developed the Metropolis Monte Carlo framework and contributed to the manuscript. A.M. and C.A.B. performed all experimental synthesis and X-ray diffraction studies. C.A.B. interpreted the X-ray diffraction and computational data, contributed to writing the manuscript and co-supervised the project. V.R.C. initiated the research concept co-developed the theoretical framework, interpreted the results, contributed to writing the manuscript and supervised the project.

COMPETING INTERESTS

The authors declare no competing interests.

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Figures

Figure 1

Predictive multiscale screening of high entropy compounds in a generic phase starting from readily available theoretical and experimental databases to screen potential elemental components. The multicomponent combinations are ranked by comparing ab initio computed enthalpy and entropy

descriptors. Candidates for further experimental synthesis are predicted from Metropolis Monte Carlo simulations by comparing the temperature and oxygen partial pressure dependent phase fraction and disorder in finite length supercells.

Figure 2

The sum of Shannon ionic radii of B-site cation and oxygen anion, $R_B + R_O$, plotted against the respective DFT computed B - O bond length for relevant cations.

Figure 3

Eight formula unit representation of (a) $A_2B_2O_7$ pyrochlore and (b) $A_2B_2O_8$ fluorite structures. A smaller, two formula unit representations are shown for (c) pyrochlore and (d) fluorite structures. A-site and B-site cations are shown in green and blue spheres within the like colored translucent polyhedra, respectively. Oxygen ions are present at the corners of each polyhedron.

Figure 4

Heat maps for mixing enthalpy in eV/B - site of La2(BB)2O7 $\neq$ $ntternary \square s \square phaseP, Hmix[A2(BB)2O_n; P]$, calculated from first principles using Eq. 1. Presented for (a) pyrochlore, (b) PRLO, (c) LaTaO4, (d) fluorite, (e) fergusonite and (f) perovskite phases. The annotation ‘G’ in each panel represents the ground state for the two cation combination. The color legend are shown separately for(a–c) and (d–f).

Figure 5

A comparison of the enthalpy and entropy descriptors, m and σ , for all 21 five component (a) $La_2B_2O_7$ and (b) $Nd_2B_2O_7$ pyrochlores. Enthalpy and entropy descriptor differences between pyrochlore and PRLO

structures, m and o, for (c) La2B2O7 and (d) Nd2B2O7 compositions. Each data point is annotated with its index.

Figure 6

Heat map of phase fraction, h_{Pi} for $\text{La}_2(\text{HfNbScSnZr})_2\text{O}_7$ is plotted as a function of $\log(p_{O_2}/p^0)$ and T . (a) pyrochlore, (b) percentage vacancies in pyrochlore structure, (c) PRLO and (d) LaTaO₄ phases. The contour lines along with their annotated values are also given for each panel.

Figure 7

Heat map of short range order parameter for selected two component combination for $\text{La}_2(\text{HfNbScSnZr})_2\text{O}_7$ is plotted in separate panel as a function of $\log(p_{O_2}/p^0)$ and T . The contour lines along with their annotated values are also given for each panel.

Figure 8

Experimental powder X-ray diffraction pattern for (a) La based five component sample and (b) Nd based five component oxide.

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