Prediction and accelerated laboratory discovery of previously unknown 18-electron ABX compounds

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Chemists and material scientists have often focused on the properties of previously reported compounds, but neglect numerous unreported but chemically plausible compounds that could have interesting properties. For example, the 18-valence electron ABX family of compounds features examples of topological insulators, thermoelectrics and piezoelectrics, but only 83 out of 483 of these possible compounds have been made. Using first-principles thermodynamics we examined the theoretical stability of the 400 unreported members and predict that 54 should be stable. Of those previously unreported 'missing' materials now predicted to be stable, 15 were grown in this study; X-ray studies agreed with the predicted crystal structure in all 15 cases. Among the predicted and characterized properties of the missing compounds are potential transparent conductors, thermoelectric materials and topological semimetals. This integrated process—prediction of functionality in unreported compounds followed by laboratory synthesis and characterization—could be a route to the systematic discovery of hitherto missing, realizable functional materials.

An interesting observation that surrounds the current compilations of structures of previously synthesized inorganic compounds is the relatively large proportion of chemically reasonable atom combinations that are not reported therein[1–3]. Some of these 'missing compounds' can be readily rationalized as being unstable for chemically obvious reasons, but it is diffi the method is conducted by applying it to previously reported compounds from the same general chemical class, and verifying that in all cases the stability and the observed low-temperature (T) structures were predicted correctly.

This approach combines the true discovery of missing compounds with the prediction of properties that are expected to be featured in chemically recognizable stable structures. Unlike approach (1), we focus on hitherto missed compounds, and unlike approaches (2) and (3), we filter out manifestly unstable compounds before advertising their interesting new properties. Unlike model stability. (2) We compared the total energy of the lowest-energy ternary structure with those of all the combinations of unary, binary and ternary competing phases.

The protocol of testing the stability of a hypothetical compound described here applies to the ground-state structure ($T = 0$), in which the stable ground states are separated out from those that are not ground states because specific competing phases or dynamic instability precludes their existence. If a compound is proved to be a ground state, it must appear in the composition–temperature phase diagram. The temperature at which it will appear may or may not be experimentally accessible, however, and a complete, finite T calculation of the phase diagram could be desirable (for example, those predicted in Mbaye et al.[36], Ferreira et al.[37] and Akbarzadeh et al.[38]). We did not attempt phase-diagram calculations here, an effort that might be done in the future. When we applied our $T = 0$ protocol to 44 compounds reported in the ICSD (Mn_2SiO_4, Sr_2TiO_4, Al_2ZnS_4, Ba_2TiS_4, Ca_2SiS_4, Sc_2MgSe_4, In_2MgTe_4[39], BaZnSi, BaZnSn, CaZnGe, AgKO, KCaBi, CuKSe, KMgAs, KMgP, KZnSb, LiAlGe, LiAlSi, LiBeN, CuLiO, LiInGe, LiMgN, LiSrSb, LiYGe, NaAlSi, RbCaAs, SrZnSi[40], TiPtGe, VCoSi, VCoGe, NbCoSi, NbCoGe, NbCoSn, NbRhSi, NbRhGe, NbRhSn, NbIrSi, NbIrGe, NbIrSn, TaCoGe, TaRhGe, TaCoSi, TaRhSi and TaIrSi), in all cases we found that we correctly predicted their stability and in the correct (observed) structure. This suggests that the $T = 0$ protocol is at least sometimes, if not often, a good predictor of laboratory existence in the said structure from these closed-shell inorganic groups, and that many such previously made compounds reported in the ICSD represent a stable ground state, not a metastable structure. Examining groups of candidate competing structures is important, as illustrated, for example, by the study of Carrete et al.[41] that overlooked a large number of unreported ABX compounds as well as previously synthesized materials. Many of these structures were disqualified from being stable because only a cubic form (often not the ground state) was allowed, which led to the very low yield (<0.1%) of material prediction out of the initial set examined, in addition to the assignment of instability on a large number of previously synthesized materials.

Previously missing now predicted stable compounds. Of the 400 missing compounds, we predict 54 to be stable in specific structures ('+' symbols in Figs 1 and 2) and the remaining 346 to be unstable in all structures examined ('–' symbols in Figs 1 and 2). The stability of four compounds is too close to determine as judged by the energy distance to the convex hull (see Methods), which is a set of triangle segments that connect the energy of a set of structures (including the elemental phase end points) that are stable with respect to separation into other structures of neighbouring compositions. The predicted stable 18-electron ABX compounds, their lowest-energy crystal structure (see Supplementary Tables 3–8 for more details) and their formation enthalpy are given in Table 1. The closest competing phases are given in Supplementary Tables 9 and 10.

Predicted compounds in new groups versus predicted compounds that supplement previously known groups. It is interesting to examine whether certain nominal 538223(smic22(5384

Zr, Hf)(Co, Rh, Ir)(P, As, Sb) group were missing, and 11 of them are now predicted to be stable (TiRhP, TiIrP, HfRhP, HfIrP, TiIrAs, ZrIrAs, HfRhAs, HfIrAs, TiIrSb, ZrIrSb and HfIrSb), which makes the subgroup almost complete. The exception is the compound ZrCoAs, which is slightly unstable with an energy distance to the strongest competing phases (see Methods) of only 11 meV atom^{-1}. Also, five out of 18 compounds in the (V, Nb, Ta)(Co, Rh, Ir)(Si, Ge) group were missing and all are now predicted to be stable (VRhSi, VIrSi, VRhGe, VIrGe and TaIrGe), thus completing the group.

Predicted trends in crystal structure types. The crystal structures of the predicted ABX compounds are given in Table 1. The labels of structure types are taken from Zhang *et al.*[40] and are listed for convenience in Supplementary Tables 1 and 2. We denote in Figs 1 and 2 compounds with the cubic LiAlSi-type structure ($F\bar{4}3m$, also called a half-Heusler structure[11,23,24,27–30]) with bold violet symbols. Some emerging structural trends are that ABX compounds with a light atom X (that is, O, S, Se, N, P, As, C, Si and Ge) tend to have non-cubic structures, whereas ABX compounds with a heavy atom X (that is, Te, Sb, Bi, Sn and Pb) tend to have a cubic structure (LiAlSi-type). For example, the predicted ABX compounds in groups IV–X–IV, IV–IX–V and V–IX–IV with the heavy X elements Sb, Bi, Sn or Pb are all cubic.

Previously missing now predicted unstable compounds. We predict that as many as 346 (85%) (four are borderline cases) of the 400 missing ABX compounds are thermodynamically unstable (shown by minus signs in Figs 1 and 2), so they are ‘missing’ for a good reason. Most of them are unstable because of competing multinary compounds (for example, CaNiO is unstable with respect to CaO + Ni). A few are unstable with respect to decomposition into the elemental phases (that is, the formation enthalpy, $\Delta H_f > 0$): AuPdCl (ΔH_f

reaction time), the compounds HfIrSb, TaIrSn, ZrIrSb, TiIrSb, ZrNiPb and HfRhP were made single phase and the powder X-ray diffraction (XRD) pattern (see Fig. 4 and Supplementary Figs 6–8) clearly validates the predicted structure. It is interesting that the single phases made so far have energy distances to the strongest competing phases (denoted as $\Delta H_f(ABX) - C(x_{ABX})$, see Methods) of less than $-0.13\,\text{eV atom}^{-1}$, whereas VIrSi and ZrRhBi, with $\Delta H_f(ABX) - C$

used in the first step of materials discovery for the selection of the predicted stable materials to be synthesized.

Trends in bandgaps. We have used hybrid functional (HSE06)[43] wave functions with spin–orbit coupling to evaluate the bandgaps of the predicted materials. Our calculations (see Table 1) show that all 18-electron ABX compounds with non-cubic structures and cubic ABX compounds with one transition-metal element are metallic. For example, the new II–X–VI (MgPdTe) and III–X–V (III = Al, Ga, In) (AlNiP, AlNiAs, AlNiSb, GaNiSb, InNiSb and InPdSb) cubic phases with only one transition-metal species are metallic. In contrast, cubic ABX compounds with two transition metals are semiconductors. This can be understood by considering the basic electronic structure of the crystal (see Fig. 5a): the transition metal atoms A and B are mutually tetrahedrally coordinated nearest neighbours. Thus, the d states of A and B, that is, T_2(A, d) and T_2(B, d) as well as E(A, d) and E (B, d) strongly couple and repel each other, which opens a large gap between the high-lying unoccupied d states and the low-lying occupied d states. A hybridized s state (labelled as a_1) resides near the band edges, as illustrated in Fig. 5a. This a_1 state can decrease if the s orbitals that constitute the state are low lying. Figure 5b–e show the calculated band structures of TaIrSn, ZrIrSb, HfIrSb and HfIrAs, which illustrates the downward shifting of the a_1 state (labelled as Γ_6^s at the Γ T609.2999395sgin112e395sd(eW(ed.2487273.42

thermopower of synthesized ZrNiPb at room temperature (r.t.) are 220.1 S cm^{-1} and –153.9 μV K^{-1}, respectively, which gives a power factor as high as 5.2 μW cm^{-1} K^{-2} (see Supplementary Table 22). For comparison, the r.t. power factors of synthesized HfIrSb and ZrIrSb are 0.22 μW cm^{-1} K^{-2} and 0.013 μW cm^{-1} K^{-2}, respectively. Analogous to the alloys of ZrNiSn and HfNiSn, for example, $Zr_{0.5}Hf_{0.5}NiSn$ with a figure of merit[45] $ZT > 0.5$ at 700 K (r.t. power factor being 3 μW cm^{-1} K^{-2}), one can use the alloys of ZrNiPb and HfNiPb that have a very small lattice mismatch (0.2%), similar to ZrNiSn and HfNiSn, to reduce thermoconductivity. Indeed, the total energy calculation of $Zr_{0.5}Hf_{0.5}NiPb$ with Zr and Hf decorated on the four equivalent A sites in the unit cell of an ABX LiAlSi-type structure shows that its formation energy relative to that of ZrNiPb and HfNiPb can be neglected (0.4 meV atom^{-1}).

Transparent conductors. As a rather rare functionality among the 18-electron ABX family recently discovered in TaIrGe[35] from an inverse design approach, we focussed on realizing more predicted transparent conductors. Three compounds (TiIrSb and ZrIrSb from the group IV–IX–V and TaIrSn from the group V–IX–IV) with wide direct bandgaps (E_g^{dir}) of 2.3~2.5 eV (similar to TaIrGe[35]) were identified as potential transparent conductors. The calculated optical absorption coefficients (α) of TiIrSb, ZrIrSb and TaIrSn (see Supplementary Fig. 5) illustrates that the optical transition across E_g^{dir} (see Table 1) is allowed and that a strong optical absorption ($\alpha = 10^6$ cm^{-1}) starts near 3 eV (for TaIrSn) or above (for TiIrSb and ZrIrSb). The many-electron multiplet effects of d–d transitions[46] –

formation enthalpy errors and the electronic structure evaluation method are also described). The crystal-structure determination is made in step (1a) by comparing the total energies of a specific ABX in a list of previously reported structure types (Supplementary Section II). The most-stable structures that emerge from the static stability test in step (1a) are tested in step (1b) by examination of their dynamic stability with phonon calculations using the density functional perturbation theory (DFPT) as implemented in Quantum Espresso[49] (Supplementary Section III). We found that all the final structures are dynamically stable, that is, have no negative phonon frequency. The static dielectric constants (including ionic contributions) are evaluated using DFPT. In a few cases, we examined whether the list of structure types used in step (1a) was not too restrictive by performing step (1c), a genetic algorithm-based structure search in which one starts from random lattice vectors and random cell positions (Supplementary Section IV). Steps (1a) and (1c) are illustrated in Supplementary Fig. 1 for HfNiPb.

Thermodynamic stability. In this step we compare the energy of the lowest-energy crystal structure of each thermodynamically stable compound with the energies of different combinations of unary, binary and ternary competing phases (described in Supplementary Section V). We use the formation enthalpies relative to elemental phases (ΔH_f) of all the competing phases to construct a 2D ‘convex hull’ denoted as $C(x)$ (illustrated by the blue lines in Supplementary Fig. 1 for an AX binary system for clarity). The energy (enthalpy) distance between the most-stable ABX to the combination of the closest competing phases, as illustrated by the red arrow in Supplementary Fig. 1, is given by $\Delta H_f(\mathrm{ABX}) - C(x_{\mathrm{ABX}})$; this is a measure of the thermodynamic stability of the ABX compound. The limitation and validation of our methodology are discussed in Supplementary Sections VI and VII, respectively.

Synthesis. The synthesis of the ABX materials was attempted by arc melting and silica-tube annealing. Stoichiometric ABX mixtures of pure elements were pellet

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