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.

n 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 therein¹⁻³. Some of these 'missing compounds' can be readily rationalized as being unstable for chemically obvious reasons, but it is difficult to speculate why many of the others are unreported. Not only could the structure and properties of such missing compounds (should they exist) improve our understanding of chemical trends within series of materials that currently feature missing entries, but the history of solid-state chemistry and material science suggests that new compounds could come with new and potentially technologically relevant functionalities. Laboratory discovery of new functional materials without prior information to narrow down the likely compositions and structures can be challenging. In addition to the large number of possible combinations of elements, unknown crystal structures can complicate the process of identification and structure determination, as one cannot a priori classify and identify a set of non-indexed diffraction peaks as belonging to a specific new phase. As a consequence, many synthetic attempts, so called 'dark reactions' that are not reported, are carried out to identify a new phase among known and unknown phases and to isolate it for further structural characterization.

Current theoretical approaches

The widespread accessibility of first-principles electronic structure codes and fast, multiprocessor computational platforms has proliferated the prediction of previously unknown thermodynamically stable compounds^{4–7} as well as separate predictions of the functionalities of materials. Three main styles of literature predictions are:

(1) The prediction of unknown properties⁸⁻¹⁵ of generally known and previously synthesized^{1,2} compounds. This includes highthroughput calculations of the properties of materials listed in databases^{9,10,13-16}. Here stability is generally taken for granted, given that the material and its crystal structures are known experimentally.

- (2) The prediction of unknown properties of artificial, non-equilibrium structures¹⁷⁻²¹ (such as superlattices and core-shell nanostructures). Here the issue of thermodynamic stability does not arise because activation barriers are presumed to be generally insurmountable under ordinary conditions.
- (3) The forecast of new properties of hypothetical compounds in presumed structures²²⁻²⁶. Here authors generally do not examine the theoretical stability of the crystal structure as their interest lies in the properties of a postulated structure.

Approach (1) runs the risk of missing potentially stable but previously overlooked unreported compounds, and approach (2) relies on protection by kinetic barriers. Approach (3) can deliver exciting predicted properties albeit in potentially unstable structures, unrealizable in practice (for example, a high-bulk modulus in PtN^{25} , optoelectronics²³, hypothetical topological insulation²⁶ and piezoelectricity²⁴ in some of the hypothetical ABX compounds). Also, 'model Hamiltonian' approaches that specify the Hamiltonian via generic interaction terms (such as spin–spin or electron–electron or electron–phonon) but do not specify the chemical and structural identity of the system (atomic numbers, composition and structure) might predict interesting generic properties, but lack a bridge to the materials in which such predicted properties will 'live'.

Here we apply another theoretical approach followed by the laboratory examination of missing compounds. Regarding the predictive theory, we examine groups of unreported (missing) compounds via first-principles thermodynamics. In this approach, the Hamiltonian is given atomic numbers, composition and structure and seeks compounds that are stable statically and dynamically with respect to competing phases. The calculation separates the 'unreported predicted stable' from the 'unreported predicted unstable' compounds, and then forecasts material properties of the stable new materials in their affirmed structures. Validation of

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	N-X-(8-N)													
	I-X-VII		II–X–VI				III-X-V				IV-	-X-I	v	
Rb Cl		Hg <mark>S</mark>		Hg Te	o	In Bi	0	La Bi	-	1 1	Hf Pb	+	+	+
K CI		Cd S		Cd Te		Ga Bi	+ - 0	Y Bi	V	1 1	Zr Pb	+	+	+
Na Cl		Zn S		Zn Te		Al Bi		Sc Bi	~	/ +	Ti Pb	-	-	-
		Ba <mark>S</mark>		Ba Te		In Sb	+ + +	La <mark>Sb</mark>	~	~ ~	Hf <mark>Sn</mark>	V	~	~
		Sr S		Sr Te		Ga <mark>Sb</mark>	+ - +	Y Sb	~	1 1	Zr Sn	V	~	~
		Ca S		Ca Te		Al Sb	+ - +	Sc Sb	~	/ /	Ti Sn	V	+	~
Ag CI		Mg <mark>S</mark>		Mg Te	- + -	In As		La As	+	/ +	HfGe	V	~	~
Cu Cl		Be S		Be Te		Ga As		YAs	+	+ 🗸	ZrGe	~	~	~
Rb F		Hg O		Hg <mark>Se</mark>		ALAs	+	ScAs	+	+ -	TiGe	~	~	
ΚF		Cd O		Cd Se			·				LIF Si			<u> </u>
Na F		Zn O		ZnSe							7. 0			
Li F		Ba O		Ba <mark>Se</mark>		GaP		TP	~	+ •			~	~
·		Sr O		Sr Se		AI P	+	Sc P	`	+ 🗸	li Si	~	~	~
		Ca O		Ca <mark>Se</mark>		In N		La N	+		Hf C		-	
Ag F		Mg O		Mg <mark>Se</mark>		Ga N		Y N	-		Zr C	-	-	
Cu F		Be O		Be Se		AI N		Sc N			Ti C	-	-	-
	Ni Pd Pt		Ni Pd Pt		Ni Pd Pt		Ni Pd Pt		Ni F	d Pt		Ni	Pd	Pt

Figure 1 | N-X-(8–N) compounds obtained by the insertion of a group X element (Ni, Pd, Pt) into an eight-valence electron lattice. The group X elements are shown in blue, N in green and (8–N) in red. Tick, previously reported compounds^{1-3,32-34}; plus sign, unreported and predicted here to be stable; minus sign, unreported and predicted here to be unstable; circle, too close to call. The compounds that have the cubic LiAlSi-type structure ($F\bar{4}3m$) are denoted by the bold violet symbols. The existing compounds appear in seven structure types; a total of 41 structure types were examined theoretically.

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 Hamiltonian approaches, we chemically and structurally identify the compound in which the predicted functionality is featured. Regarding the laboratory examination, we build on the aforementioned theory that first determines which compounds are stable, second predicts their crystal structures (and thereby provides information that allows chemists to perform a directed rational synthesis and structure identification in multiphasic samples as well as a structure refinement) and third allows one to select the candidate compounds that exhibit the most interesting properties. We illustrate how the iteration between experiments and theory greatly accelerates the discovery of novel materials that have interesting functionalities.

The 18-valence electron ABX system

We illustrate this approach to the discovery of missing functional materials by considering the 18-valence electron ABX family in which many interesting properties have been identified^{16,24,26–30}. The ternary eight-electron ABX compounds are an extension of the well-known binary eight-electron AX semiconductors with the closed shell s^2p^6 (octet rule³¹), such as II–VI (for example, ZnO), III–V (for example, GaAs) or IV–IV (for example, SiC), obtained by splitting the cation in AX into two cations in ABX, such as II–VI becoming I–I–VI or III–V becoming I–II–V. The 18-electron ABX compounds are a conceptual extension to the eight-electron AX by the insertion of a group X element (Ni, Pd, Pt) with *d*

valence electrons into an eight-valence electron lattice (Fig. 1), or by inserting a group IX element (Co, Rh, Ir) into the nine-valence electron lattice (Fig. 2). Previously reported ABX compounds exist in ~40 different structure types, including the cubic LiAlSi-type structure $(F\bar{4}3m)$ and the orthorhombic MgSrSi-type structure (Pnma). Curiously, however, of the 483 ABX 18-electron materials that could be conceived from these groups, only 83 have been made previously (ticks in Figs 1 and 2); the remaining 400 are unreported in compilations of synthesized systems, such as the Inorganic Crystal Structure Database (ICSD)¹, International Centre For Diffraction Data Powder Diffraction File² and Villars and Calvert³, as well as in additional journal publications known to us³²⁻³⁴. In fact, the entire I-X-VII, II-X-VI, II-IX-VII and III-IX-VI subgroups of the 18-electron ABX family are not documented. Yet, the known compounds from these ABX groups include interesting functionalities, such as thermoelectricity³⁰, piezoelectricity²⁴, topological band structure properties (mostly from the III-X-V group)²⁶⁻²⁹ and p-type transparent conductivity³⁵, which raises the prospects that the missing compounds from these groups may have interesting properties.

Results and discussion

Determination of stability versus instability of hitherto missing compounds. Using first-principles density functional theory (DFT), we examined the thermodynamic stability of each missing 18-electron ABX compound with respect to other crystal structures (including of different stoichiometry), stability with respect to decomposition into any combination of their constituents and dynamic (phonon) stability. We addressed the stability of a missing ABX compound within DFT in two steps. (1) We determined the lowest-energy crystal structure among the many possibilities, which is a dedicated problem in itself, both via a genetic algorithm that uses techniques inspired by natural evolution, such as mutation and selection, and via a fixed list of structure types (Supplementary Tables 1 and 2), including phonon



Figure 2 | (N+1)-IX-(8–N) compounds obtained by the insertion of a group IX element (Co, Rh, Ir) into a nine-valence electron lattice. The group IX elements are shown in blue, (N+1) in green and (8–N) in red. Tick, previously reported^{1-3,32-34}; plus sign, unreported and predicted here to be stable; minus sign, unreported and predicted here to be unstable; circle, too close to call. The compounds that have the cubic LiAlSi-type structure ($F\bar{4}3m$) are denoted by the bold violet symbols.

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 compositiontemperature 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, SrZnSi40, 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 chemical groups are missing for a good reason. Groups I–X–VII, II–X–VI, II–IX–VII and III–IX–VI, and subgroup III–X–V (III = Al, Ga, In) are thus included in our study even though they previously did not contain a single reported member (that is, being missing groups). We predict ten stable compounds from subgroup III–X–V (III = Al, Ga, In) (GaNiBi, InNiSb, InPdSb, InPtSb, GaNiSb, GaPtSb, AlNiSb, AlPtSb, AlNiAs and AlNiP), three from group III–IX–VI (GaIrTe, AlIrSe and ScRhTe) and one from II–X–VI (MgPdTe). The remaining 40 missing now-predicted stable compounds belong to groups that contained some known members. For example, 12 out of the 27 compounds in the (Ti,

Compounds	Structure (space group)	Lattice constant (Å)	$\Delta H_{\rm f}$ (eV atom ⁻¹)	$E_{\rm g}(E_{\rm g}^{\rm dir})$ (eV)	ε_0
ScPtBi	s1 (F43m)	6.557	-0.86	0.00 (0.00)	157.90
TiPdSn	s1 (F43m)	6.230	-0.52	0.74 (1.59)	21.61
ZrNiPb	s1 (F43m)	6.267	-0.65	0.43 (0.87)	22.22
ZrPdPb	s1 (F43m)	6.506	-0.68	0.53 (1.09)	21.67
ZrPtPb	s1 (F43m)	6.518	-0.84	1.01 (1.93)	19.74
HfNiPb	s1 (F43m)	6.252	-0.57	0.32 (1.05)	22.32
HfPdPb	s1 (F43m)	6.485	-0.59	0.49 (1.30)	22.51
HfPtPb	s1 (F43m)	6.485	-0.77	0.97 (1.31)	21.41
ScRhTe	s1 (F43m)	6.350	-1.05	0.75 (0.75)	17.87
TilrAs	s1 (F43m)	5.941	-0.70	1.40 (1.40)	17.54
TilrSb	s1 (F43m)	6.169	-0.76	1.63 (2.39)	16.05
ZrRhBi	s1 (F43m)	6.462	-0.71	1.28 (1.59)	17.93
ZrlrAs	s1 (F43m)	6.182	-0.99	0.78 (0.78)	18.41
ZrlrSb	s1 (F43m)	6.372	-1.11	1.91 (2.25)	15.11
ZrlrBi	s1 (F43m)	6.496	-0.76	0.71 (0.71)	20.83
HfRhBi	s1 (F43m)	6.455	-0.64	0.60 (0.60)	23.29
HflrAs	s1 (F43m)	6.159	-0.96	0.00 (0.00)	115.13
HflrSb	s1 (F43m)	6.345	-1.07	1.49 (1.49)	15.45
HflrBi	s1 (F43m)	6.476	-0.71	0.00 (0.00)	89.32
TaCoSn	s1 (F43m)	5.974	-0.29	1.37 (1.63)	20.13
TaRhSn	s1 (F43m)	6.201	-0.48	1.40 (1.76)	18.32
TalrGe	s1 (F43m)	6.026	-0.75	1.62 (2.49)	16.86
TalrSn	s1 (F43m)	6.233	-0.67	1.55 (2.26)	16.93

Table 1 | Physical parameters for the predicted stable ABX semiconductors and semimetals.

Lowest-energy structure, lattice constant and formation enthalpy (ΔH_i) from DFT, fundamental bandgap (E_g^i) and direct bandgap (E_g^{dr}) from hybrid functional (HSE06) with spin-orbit coupling, as well as the static dielectric constant (e_0) from the DFPT of the predicted stable ABX semiconductors or semimetals. The predicted stable metals are distributed in eight structure types (see Supplementary Tables 1, 2 and 19): the LiAISi type (MgPdTe, AlNiP, AlNiAS, AlNiSb, GaNiSb, InNiSb and InPdSb), the MgSrSi type (GaPtSb, InPtSb, ScNiAS, ScPdP, ScPdAS, YNiAS, YPdAS, LaPtAS, TiRhP, TilrP, HfRhP, HfRhAS, VRAS, VRAS, VRAS, VISA, Marker 1, and VIrGe), the ZrBGSi type (YPdP and LaNiAS), the CaPdSi type (GaNiBi and AllrSe), the CorV type (LaNiN), the LiBeN type (GaIrTe), the AdEUGe type (HIfrP) and the SrmSi-type (AIPSD).

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 (F43m, 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 ($\Delta H_f = 0.03 \text{ eV} \text{ atom}^{-1}$), AuPtCl (0.12 eV atom⁻¹), InNiN (0.08 eV atom⁻¹), InPdN (0.14 eV atom⁻¹), InPtN (0.15 eV atom⁻¹), VCoPb (0.17 eV atom⁻¹), VRhPb (0.03 eV atom⁻¹) and a borderline case, VRhC (0.01 eV atom⁻¹).

tes previous theoretical study to predict interesting physical properties²⁴. These are unlikely to materialize with standard growth methods. Ir) **Trends in thermodynamic stability when varying anions or** cations. We found that all the cathides and almost all the nitrides

Some of the compounds now predicted to be unstable (for

example, CaNiO, SrPtSe and BaPdTe) were the subject of a

cations. We found that all the carbides and almost all the nitrides (except LaNiN, which is slightly stable) are thermodynamically unstable, in sharp contrast with the number of stable compounds with the less ionic heavier anions, which indicates that ionicity is not preferred in these 18-electron ABX compounds. Comparing the two subgroups of III–X–V with III = Al, Ga, In versus III = Sc, Y, La, we found that the former subgroup was completely missing in the literature, and after our prediction it still has fewer stable compounds than the latter subgroup. The key factor is that in the III–X–V group with III = Sc, Y, La there are two transition-metal species with *d* orbitals that hybridize and repel, displacing the occupied *d* bands to a lower energy and thus stabilizing the compound. In contrast, the former subgroup contains only one transition-metal species and therefore lacks the energy stability of *d*–*d* bonding.

Laboratory synthesis of as yet unreported compounds now predicted to be stable. Our first synthetic targets in the challenge of experimental verification were those compounds in the two most-populated structure types, the cubic LiAlSi-type and orthorhombic MgSrSi-type structures (see Supplementary Table 1). Among these groups, many compounds were also not attempted owing to reagent toxicity (for example, the arsenides) or weak predicted thermodynamic stability (that is, energetic distance from the convex hull). Attempts to synthesize the predicted stable compounds in powder form were made using arc melting and quartz-tube annealing, two of many synthetic techniques available to make new materials. Figure 3 shows the realized single phasic versus multiphasic compounds. After optimization of the synthesis conditions (such as temperature and



Figure 3 | The 18-electron ABX compounds predicted by theory and synthesized in this work. $\Delta H_f(ABX) - C(x_{ABX})$ is the energy distance to the strongest competing phases, where ΔH_f is the formation enthalpy and C(x)denotes the convex hull considering competing phases (see Methods). <*Z>* is the average atomic number. Square, cubic LiAlSi-type ($F\bar{4}3m$) structure; triangle, orthorhombic MgSrSi-type (*Pnma*) structure. Filled symbol, single phase; open symbol, multiphase. VIrSi and ZrRhBi are multiphases with high purity (see the Supplementary Information). Dashed line (at $\Delta H_f(ABX) - C(x_{ABX}) = -0.13 \text{ eV}$ atom⁻¹), diagrammatical separation of single-phase and multiphase compounds (one error, VIrSi, out of 15 cases). Red symbol, with measured properties (see Supplementary Tables 21 and 22); blue symbol: properties not measured.

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 $-0.13 \text{ eV} \text{ atom}^{-1}$, whereas VIrSi and ZrRhBi, with $\Delta H_f(ABX) - C(x_{ABX}) \leq -0.13 \text{ eV} \text{ atom}^{-1}$, were made with high purity in multiphasic products. The other multiphasic compounds made, ScRhTe, ScPtBi, VRhSi, ScPdP, ZrIrBi, TiIrP and ZrPdPb, have weaker thermodynamic stability and were selected to test the theoretical predictions. We learned that certain compounds with a very weak stability are hard to make even in multiphasic mixtures because all the attempts to synthesize AlNiP and InNiBi were unsuccessful.

Transmission electron microscopy (TEM) was used to confirm the crystal structure and composition of all the new phase-pure and multiphase samples. The structures of single crystallites were confirmed by selected area electron diffraction (SAED). The chemical composition was confirmed by energy-dispersive X-ray spectroscopy (EDS). We illustrate TEM measurements for HfIrSb in Fig. 4 and for all the other materials in the Supplementary Information (Supplementary Figs 9-23). For all nine multiphase samples (ScRhTe, ZrRhBi, ScPtBi, VRhSi, VIrSi, ScPdP, ZrIrBi, TiIrP and ZrPdPb) the diffraction pattern simulated from the predicted crystal structure enables the direct identification of the new material in a mixture of known or even unknown phases. The 15 missing yet unreported materials synthesized here plus the additional TaIrGe and TaCoSn synthesized previously^{35,42} all crystallized in their predicted crystal structures, which thus validates the theoretical procedure used. The deviations of measured versus predicted lattice parameters (typically within 1-2%) are shown in the Supplementary Information. This is a high success rate given that each compound could exist in at least one of ~40 possible structure types (by analogy with other ABX cases) and that 15 out of the 15 materials made adopted the predicted structure with lattice parameters extremely close to those predicted.

Some of the newly synthesized materials have compositions and structures that are non-trivial to guess intuitively. Contrary to the case of the synthesis of ScPtBi, which is intuitive (as its neighbouring compounds ScNiBi and ScPdBi have been reported previously (Fig. 1)), the synthesis of 1:1:1 ScRhTe was not obvious because no compound has been reported previously in the III–IX–VI family, in which a large majority of the compositions are predicted to be unstable (Fig. 2). Interestingly, the predicted stable ScRhTe could be synthesized and the predicted unstable ScIrTe could not be synthesized by similar approaches, consistent with theory. Moreover, attempts to synthesize the predicted unstable VRhSn, InPdBi, MgNiTe, NbCoPb, VCoPb, VIrSn, MgNiS and MgPdS were also unsuccessful.

Combination of synthesis with theoretical prediction accelerates each step of the experimental discovery process. The first step in the discovery of new functional materials is to select the reactants and their ratios. During the past decades, chemists have developed empirical and semiempirical rules to narrow the large number of possible Daltonian stoichiometries of elements that can be imagined. However, chemical intuition may not always hit the mark so synthetic attempts guided by such intuition may fail without providing indications as to the source of failure. From the prediction, useful information about the stability of the materials in comparison to that of their competitors can be rationalized. The instability of materials can be identified and understood and the stability of counterintuitive materials can be highlighted. It is important that the comparison with competitors improves the efficiency of the predictive theory and provides the experimentalist with a success rate and, in some cases, growth conditions.

Newly made solid samples are often multiphasic. Thus, most methods to synthesize new materials lead to polycrystalline samples with a mixture of known and unknown phases. Using XRD, the experimentalists can identify the newly made compound by isolating the diffraction peaks that belong to this phase in a deductive manner. This work is realized by identifying the other known phases of the sample and also distinguishing the peaks that cannot be indexed using the powder-diffraction databases. However, the new phase cannot be identified among other unknown phases. In this context, the theoretical approach used here provides useful information: the predicted crystal structure. The diffraction pattern simulated from the predicted crystal structure enables the direct identification of the new material in a mixture of known or even unknown phases. The acceleration of identification (and also of refinement) is enabled by the accuracy of the prediction of the symmetries (unit-cell parameters are usually less than 2-3% off).

Functionality of new materials. In the inverse design search for compounds with target functionality we (1) select a broad chemical group within the database of previously made compounds, (2) construct a metric that reflects the target functionality and (3) search the database for material that follows this functionality metric. Left out of this procedure are materials not listed in database because they were never made. Here we augment the database of previously made compounds with those 'missing compounds' predicted to be thermodynamically stable, which ensures that the search for target functionality is not just among the 'usual suspects' materials. Furthermore, the characterization of the properties of new materials is accelerated owing to the calculation of their functionalities. The prediction highlights the most interesting properties of the materials on which the experimentalists will focus. This information is also



(110) zone

Figure 4 | **Discovery of the HflrSb ternary material. a**, Rietveld refinement carried out on the pure sample obtained after annealing under vacuum at 1,050 °C. Red points, observed XRD intensity; black curve, calculated intensity; blue curve, difference between observed and calculated intensities; green line, Bragg positions; black labels, corresponding lattice plane. a.u., arbitrary units. **b**, SAED and EDS experiments further confirmed the predicted crystal structure (LiAlSi-type, $F\bar{4}3m$) (for more details, see Supplementary Information).

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 a₁ state (labelled as Γ_6^s at the Γ point) relative to the $\Gamma_8^{p,d}$ state (belonging to the hybridized t_2 state in Fig. 5a) at Γ . In HfIrAs, the Γ_6^s state drops below the $\Gamma_8^{p,d}$ state (similarly for HfIrBi, see Supplementary Fig. 3), and this band inversion leads to a topological phase transition, as found for ScPtBi in another study²⁷ in an assumed structure. We have confirmed, ex post facto, the stability of that structure type and confirmed its band inversion (see Supplementary Fig. 4). The non-monotonic trends for the HfIr(As, Sb, Bi) subgroup, which reflect that the drop of the Γ_6^s state can be induced by either a relativistic effect of the heavy elements (for example, Hg in HgTe⁴⁴ or Bi in ScPtBi and HfIrBi) or low-lying s orbitals of the low-Z elements (for example, As in HfIrAs compared to Sb in HfIrSb). The predicted topological semimetals provide a platform for designing new topological insulators by the application of quantum confinement (for example, on HgTe⁴⁴) or strain (for example, on ScPtBi²⁷).

Thermoelectric materials. From the 20 semiconductors predicted here (see Table 1), we found three as yet unreported 18-electron ABX compounds with small fundamental bandgaps ($E_{\rm g}$ < 0.5 eV): ZrNiPb, HfNiPb and HfPdPb. Among these, ZrNiPb is made single phase. The measured electron conductivity and



Figure 5 | Electronic structure of 18-electron ABX in the cubic LiAlSi-type structure (F43m). a, Schematic energy-level diagram of 18-electron ABX cubic structures. In this structure, all the atomic sites have T_d symmetry, and thus the d orbitals split into the T_2 and E states and the p orbitals are in the T_2 states. The states with the same symmetry (T_2 or E) hybridize with each other (the p orbitals of A and B are high lying). As A and B are nearest neighbours, their T₂ states (or E states) strongly couple and repel each other. The 18-valence electrons occupy the low-lying hybridized a1 (s) state (not shown in the diagram) mainly from the s orbital of atom X, the *p*-dominated hybridized t_2 state and the *d*-dominated t_2 and e states. Another hybridized s state (a1 in the diagram) is usually unoccupied. This a1 state can drop down if the constituent s orbitals are low lying, which leads to a potential topological phase transition. **b-e**, Band structures of TalrSn (**b**), ZrIrSb (**c**), HfIrSb (**d**) and HfIrAs (**e**) from a hybrid functional (HSE06) with spin-orbit coupling, which illustrate the decreasing of the a1 state and the topological phase transition.

thermopower of synthesized ZrNiPb at room temperature (r.t.) are 220.1 S cm⁻¹ and -153.9 μ V K⁻¹, respectively, which gives a power factor as high as 5.2 μ W cm⁻¹ K⁻² (see Supplementary Table 22). For comparison, the r.t. power factors of synthesized HfIrSb and ZrIrSb are 0.22 μ W cm⁻¹ K⁻² and 0.013 μ W 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 merit⁴⁵ ZT > 0.5 at 700 K (r.t. power factor being 3 μ W 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 TaIrGe³⁵ 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

TaIrGe³⁵) 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_{α}^{dir} (see Table 1) is allowed and that a strong optical absorption $(\alpha = 10^6 \text{ cm}^{-1})$ starts near 3 eV (for TaIrSn) or above (for TiIrSb and ZrIrSb). The many-electron multiplet effects of d-d transitions⁴⁶ that are not included in our calculations could, in principle, limit the transparency of TiIrSb, ZrIrSb and TaIrSn. The strong absorption peaks above 3 eV are seen in the optical absorption spectra of TiIrSb and ZrIrSb, obtained from ultraviolet-visible diffuse reflectance measurements (see Supplementary Table 21). The measured optical gaps of TiIrSb (2.4 eV), ZrIrSb (1.9 eV) and TaIrSn (2.4 eV) are close to the predicted direct bandgaps (omitting d-d multiplet effects) listed in Table 1, which suggests minor multiplet corrections in this range. Interestingly, the large predicted and measured gaps are greater than expected from compounds made of elements with such large atomic numbers. We measured the electrical conductivity of ZrIrSb as a representative of the predicted potential transparent conductors using the Van der Pauw method at r.t. It was found that ZrIrSb is of p-type with a hole conductivity as high as 6.5 S cm⁻¹ (see Supplementary Table 22), which is much higher than that of TaIrGe $(0.35 \text{ S cm}^{-1})^{35}$ and of the first p-type transparent conductor $CuAlO_2$ (1 S cm⁻¹)⁴⁷. The experimental measurements on standard properties that are, however, hard to evaluate from DFT theory (for example, conductivity) further highlight the predicted functional materials.

Conclusions

A systematic search of missing materials using first-principles thermodynamics readily iterated with experimental realization holds several advantages. (1) It provides guidelines as to which of the previously overlooked materials will probably be stable in a predicted structure with specified materials properties. It could significantly narrow the range of materials that need to be targeted experimentally for given functionalities (transparent conductors and topological semimetals). (2) The method also provides the identity of the low-lying competing phases, and thereby allows the future development of synthetic strategies that would destabilize such competing phases. (3) The approach naturally completes the chemical series for missing material entries, and thus establishes a sounder basis for distilling chemical rules and regularities. (4) The first-principles thermodynamics protocol we use allows us to establish, in many cases, the reason behind the instability of groups of missing compounds. (5) The approach might discourage the practice of studying theoretically exciting physical properties of hypothetical compounds and structures that can be shown by the current protocol to be manifestly unstable, and thereby reduce experimental trial and error. (6) The information provided by theory regarding the stable crystal structure could accelerate the laboratory identification of the structure from the measured XRD pattern. Indeed, the inverse XRD problem (going from a measured XRD pattern to a deduced crystal structure) is not usually straightforward for experimentalists, and often many guesses as to the structure type have to be attempted.

Here our theoretical result provides an excellent starting model. Fifteen missing ABX materials were synthesized in their predicted crystal structures and, for selected examples, their predicted physical properties were confirmed. We believe this method could direct the experimentalist towards realistic targets and allow materials to be discovered more quickly and efficiently.

Methods

Theoretical determination of crystal structure. In this step we aim to find the structure of ABX that has the lowest total energy at T = 0. The total energy is calculated in the framework of DFT using the Vienna *ab-initio* simulation package (VASP)⁴⁸ (Supplementary Section I, in which our systematic correction to DFT

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 Espresso⁴⁹ (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 $\Delta H_f(ABX) - C(x_{ABX})$; 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 pressed prior to synthesis. Arc-melting syntheses were performed in a Compact Arc-Melter MAM-1 under argon. The annealing was realized by heating the samples in sealed silica tubes under vacuum at temperatures between 500 °C and 1,100 °C. These tubes were carbon-coated to avoid oxidation of the samples. The synthesized samples were analysed by powder XRD in a Rigaku Ultima IV by $\theta/2\theta$ scanning with a step size of 0.02°. The SAED and EDS experiments were conducted using a JEOL 2100 microscope operated at 200 keV. The simulations of electron-diffraction patterns were conducted using SingleCrystal software.

Optical measurement. Diffuse reflectance measurements were performed using a Lambda 1050 UV/Vis/NIR spectrophotometer with an integrating sphere attachment (PerkinElmer). Spectra were taken from 250 to 2500 nm and two baseline spectra, at 0 and 100% reflectance, were taken using pressed polytetrafluoroethylene powder compacts. The diffuse reflectance spectra were converted into optical absorption spectra by the Kubelka–Munk relation⁵⁰ and the bandgaps estimated with Tauc plots⁵¹.

Electrical measurement. The conductivity and thermopower of sintered materials were measured at ambient conditions using methods described in detail by Hong *et al.*⁵². The measured conductivities were corrected for porosity by the Bruggemann symmetric model⁵³ and for the geometry of the sample, as outlined by Smits⁵⁴.

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References

- 1. FIZ Karlsruhe. Inorganic Crystal Structure Database (Karlsruhe, 2006).
- Kabekkodu, S. Powder Diffraction File (International Centre for Diffraction Data, 1997).
- Villars, P. & Calvert, L. D. Pearson's Handbook of Crystallographic Data for Intermetallic Phases (ASM International, 1991).
- Bloch, J. et al. Prediction and hydrogen acceleration of ordering in ironvanadium alloys. Phys. Rev. Lett. 108, 215503 (2012).
- Feng, J., Hennig, R. G., Ashcroft, N. W. & Hoffmann, R. Emergent reduction of electronic state dimensionality in dense ordered Li–Be alloys. *Nature* 451, 445–448 (2008).
- Lu, Z. W., Wei, S-H., Zunger, A., Frota-Pessoa, S. & Ferreira, L. G. First-principles statistical mechanics of structural stability of intermetallic compounds. *Phys. Rev. B* 44, 512–544 (1991).
- Pickard, C. J. & Needs, R. J. Structure of phase III of solid hydrogen. *Nature Phys.* 3, 473–476 (2007).
- Ceder, G. Opportunities and challenges for first-principles materials design and applications to Li battery materials. *Mater. Res. Soc. Bull.* 35, 693–701 (2010).
- Greeley, J., Jaramillo, T. F., Bonde, J., Chorkendorff, I. & Nørskov, J. K. Computational high-throughput screening of electrocatalytic materials for hydrogen evolution. *Nature Mater.* 5, 909–913 (2006).
- Hautier, G. et al. Phosphates as lithium-ion battery cathodes: an evaluation based on high-throughput ab initio calculations. Chem. Mater. 23, 3495–3508 (2011).

- Katsnelson, M. I., Irkhin, V. Y., Chioncel, L., Lichtenstein, A. I. & de Groot, R. A. Half-metallic ferromagnets: from band structure to many-body effects. *Rev. Mod. Phys.* 80, 315–378 (2008).
- Nielsen, M. D., Ozolins, V. & Heremans, J. P. Lone pair electrons minimize lattice thermal conductivity. *Energy Environ. Sci.* 6, 570–578 (2013).
- 13. Wang, S., Wang, Z., Setyawan, W., Mingo, N. & Curtarolo, S. Assessing the thermoelectric properties of sintered compounds via high-throughput *ab-initio* calculations. *Phys. Rev. X* **1**, 021012 (2011).
- Yang, K., Setyawan, W., Wang, S., Nardelli, M. D. & Curtarolo, S. A search model for topological insulators with high-throughput robustness descriptors. *Nature Mater.* 11, 614–619 (2012).
- Yu, L. & Zunger, A. Identification of potential photovoltaic absorbers based on first-principles spectroscopic screening of materials. *Phys. Rev. Lett.* 108, 068701 (2012).
- Curtarolo, S. et al. The high-throughput highway to computational materials design. Nature Mater. 12, 191–201 (2013).
- Butler, W. H., Zhang, X-G., Schulthess, T. C. & MacLaren, J. M. Spin-dependent tunneling conductance of Fe/MgO/Fe sandwiches. *Phys. Rev. B* 63, 054416 (2001).
- Chen, H. et al. Carbonophosphates: a new family of cathode materials for Li-ion batteries identified computationally. Chem. Mater. 24, 2009–2016 (2012).
- d'Avezac, M., Luo, J. W., Chanier, T. & Zunger, A. Genetic-algorithm discovery of a direct-gap and optically allowed superstructure from indirect-gap Si and Ge semiconductors. *Phys. Rev. Lett.* 108, 027401 (2012).
- Li, Q. et al. Superhard and superconducting structures of BC5. J. Appl. Phys. 108, 023507 (2010).
- Sofo, J. O., Chaudhari, A. S. & Barber, G. D. Graphane: a two-dimensional hydrocarbon. *Phys. Rev. B* 75, 153401 (2007).
- Badzian, A. & Badzian, T. Recent developments in hard materials. Int. J. Refract. Metals Hard Mater. 15, 3–12 (1997).
- Gruhn, T. Comparative *ab initio* study of half-Heusler compounds for optoelectronic applications. *Phys. Rev. B* 82, 125210 (2010).
- Roy, A., Bennett, J. W., Rabe, K. M. & Vanderbilt, D. Half-Heusler semiconductors as piezoelectrics. *Phys. Rev. Lett.* **109**, 037602 (2012).
- 25. Sahu, B. R. & Kleinman, L. PtN: a zinc-blende metallic transition-metal compound. *Phys. Rev. B* **71**, 041101 (2005).
- Vidal, J., Zhang, X., Yu, L., Luo, J-W. & Zunger, A. False-positive and falsenegative assignments of topological insulators in density functional theory and hybrids. *Phys. Rev. B* 84, 041109 (2011).
- 27. Chadov, S. *et al.* Tunable multifunctional topological insulators in ternary Heusler compounds. *Nature Mater.* **9**, 541–545 (2010).
- Lin, H. *et al.* Half-Heusler ternary compounds as new multifunctional experimental platforms for topological quantum phenomena. *Nature Mater.* 9, 546–549 (2010).
- 29. Xiao, D. *et al.* Half-Heusler compounds as a new class of three-dimensional topological insulators. *Phys. Rev. Lett.* **105**, 096404 (2010).
- Yang, J. et al. Evaluation of half-Heusler compounds as thermoelectric materials based on the calculated electrical transport properties. Adv. Funct. Mater. 18, 2880–2888 (2008).
- Abegg, R. Die Valenz und das periodische System. Versuch einer Theorie der Molekularverbindungen. Z. Anorg. Chem. 39, 330–380 (1904).
- 32. Hohl, H. et al. New compounds with MgAgAs-type structure: NbIrSn and NbIrSb. J. Phys. A 10, 7843-7850 (1998).
- 33. Haase, M. G., Schmidt, T., Richter, C. G., Block, H. & Jeitschko, W. Equiatomic rare earth (Ln) transition metal antimonides LnTSb (T = Rh, Ir) and bismuthides LnTBi (T = Rh, Ni, Pd, Pt). J. Solid State Chem. 168, 18–27 (2002).
- Casper, F., Seshadri, R. & Felser, C. Semiconducting half-Heusler and LiGaGe structure type compounds. *Phys. Status Solidi A* 206, 1090–1095 (2009).
- Yan, F. *et al.* Design of TalrGe: a ternary half-Heusler transparent hole conductor. Preprint at http://arXiv:1406.0872 (2014).
- Mbaye, A. A., Ferreira, L. G. & Zunger, A. First-principles calculation of semiconductor-alloy phase diagrams. *Phys. Rev. Lett.* 58, 49–52 (1987).
- Ferreira, L. G., Wei, S-H. & Zunger, A. First-principles calculation of alloy phase diagrams: the renormalized-interaction approach. *Phys. Rev. B* 40, 3197–3231 (1989).
- Akbarzadeh, A. R., Ozoliņš, V. & Wolverton, C. First-principles determination of multicomponent hydride phase diagrams: application to the Li–Mg–N–H system. Adv. Mater. 19, 3233–3239 (2007).
- Zhang, X., Stevanovic, V., d'Avezac, M., Lany, S. & Zunger, A. Prediction of A₂BX₄ metal-chalcogenide compounds via first-principles thermodynamics. *Phys. Rev. B* 86, 014109 (2012).
- 40. Zhang, X., Yu, L., Zakutayev, A. & Zunger, A. Sorting stable versus unstable hypothetical compounds: the case of multi-functional ABX half-Heusler filled tetrahedral structures. *Adv. Funct. Mater.* **22**, 1425–1435 (2012).
- Carrete, J., Li, W., Mingo, N., Wang, S. & Curtarolo, S. Finding unprecedentedly low-thermal-conductivity half-Heusler semiconductors via high-throughput materials modeling. *Phys. Rev. X* 4, 011019 (2014).
- Zakutayev, A. *et al.* Theoretical prediction and experimental realization of new stable inorganic materials using the inverse design approach. *J. Am. Chem. Soc.* 135, 10048–10054 (2013).

NATURE CHEMISTRY DOI: 10.1038/NCHEM.2207

- 43. Heyd, J., Scuseria, G. E. & Ernzerhof, M. Erratum: 'Hybrid functionals based on a screened Coulomb potential'. *J. Chem. Phys.* **124**, 219906 (2006).
- König, M. et al. Quantum spin Hall insulator state in HgTe quantum wells. Science 318, 766–770 (2007).
- Sakurada, S. & Shutoh, N. Effect of Ti substitution on the thermoelectric properties of (Zr,Hf)NiSn half-Heusler compounds. *Appl. Phys. Lett.* 86, 082105 (2005).
- Fazzio, A., Caldas, M. J. & Zunger, A. Many-electron multiplet effects in the spectra of 3*d* impurities in heteropolar semiconductors. *Phys. Rev. B* 30, 3430–3455 (1984).
- Kawazoe, H. *et al.* p-type electrical conduction in transparent thin films of CuAlO₂. *Nature* **389**, 939–942 (1997).
- Kresse, G. & Furthmüller, J. Efficiency of *ab-initio* total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* 6, 15–50 (1996).
- Giannozzi, P. et al. QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. J. Phys. A 21, 395502 (2009).
- 50. Kubelka, P. & Munk, F. Ein beitrag zur Optik der Farbanstriche. Z. Tech. Phys. 12, 593–604 (1931).
- Tauc, J. Optical properties and electronic structure of amorphous Ge and Si. Mater. Res. Bull. 3, 37–46 (1968).
- Hong, B-S., Ford, S. J. & Mason, T. O. Equilibrium electrical property measurements in electroceramics. *Key Engineering Mater.* 125–126, 163–186 (1996).
- McLachlan, D. S., Blaszkiewicz, M. & Newnham, R. E. Electrical resistivity of composites. J. Am. Ceram. Soc. 73, 2187–2203 (1990).

54. Smits, F. M. Measurement of sheet resistivities with the four-point probe. Bell System Tech. J. 37, 711–718 (1958).

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Author contributions

X.Z. performed the stability calculations as well as property calculations other than the phonon and dielectric constants carried out by L.Y. R.G., Y.L., L.H., T.O.L.S. and D.C. performed the synthesis and characterization of new ABX materials. The experimental work was supervised by K.R.P. Furthermore, X.Z., R.G. and L.Y. contributed to the writing of the paper. K.R.P. and A.Z. directed the analysis of the results and writing of the paper.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to K.R.P. and A.Z.

Competing financial interests

The authors declare no competing financial interests.