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TOPICAL REVIEW — Physics research in the materials genome

Theoretical design of multifunctional half-Heusler materials based on first-principles calculations*

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The family of *ABX* half-Heusler materials, also called filled-tetrahedral structures, is a special class of ternary compounds hosting a variety of material functionalities including thermoelectricity, topological insulation, magnetism, transparent conductivity and superconductivity. This class of compounds can be derived from two substitution approaches, *i.e.*, from Heusler materials by removing a portion of atoms forming *ordered vacancies* thus becoming half-Heusler, or from tetrahedral zinc blende compounds by adding atoms on the interstitial sites thus become *filled*-tetrahedral structures. In this paper, we briefly review the substitution approaches for material design along with their application in the design of half-Heusler compounds; then we will review the high-throughput search of new half-Heusler filled-tetrahedral structures and the study of their physical properties and functionalities.

Keywords: density functional theory, high-throughput materials prediction, half-Heusler, transparent conductor

PACS: 71.15.Nc, 71.20.Lp, 71.20.Ps **DOI:** 10.1088/1674-1056/27/12/127101

1. Introduction

Along with the fast development of computation resources and methods, materials design has become a substantial method for searching physically interesting and technologically critical functional materials. Diamond-like semiconducting compounds such as Si and GaAs (a synthetic material designed in laboratory[1]) formed by two sets of face-centered cubic (fcc) sub-lattices are one of the most significant classes of materials for industry, which are essential for information, electrical, energy, healthcare and aerospace technologies.[2–8] This class of materials has been the focus of materials design[9–11] due to the quest of new technologically useful semiconductors. The group of Heusler compounds formed by four sets of fcc sub-lattices shows broad variety of physical properties, including half-metallicity,[12] Kondo effect,[13] superconductivity,[14] topological insulation,[15] and magnetic topological Weyl fermion.[16] The family of half-Heusler compounds with three sets of face-centered sub-lattices are closely related to both diamond-like and Heusler materials. As illustrated in Fig. 1, half-Heuslers can be derived from diamond-like structures by filling the third fcc sub-lattice forming the filled-tetrahedral structures (FTSs),[17] or from Heuslers by removing the atoms on the fourth fcc lattice forming ordered vacancy compounds (OVCs) (OVCs were studied in many other structure types[10,18]). Being derivatives of both diamond-like and Heusler materials,

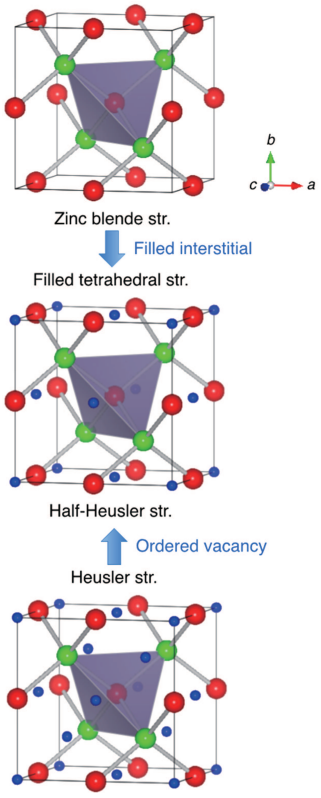


Fig. 1. (color online) Derivation of the half-Heusler filled tetrahedral structure (space group: F-43m) from the zinc blende structure (F-43m) or the Heusler structure (Fm-3m).

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half-Heuslers show a variety of materials functionalities including semiconductivity,[17,19] thermoelectricity,[20–25] topological insulation,[26–29] magnetism,[30,31] transparent conductivity,[32] and unconventional superconductivity,[33] as well as Rashba spin splitting,[34] strain-tolerant flexible inorganics,[35] topological Dirac semimetallicity,[36] *etc*. in their relative ternary systems.[37–42] Therefore, it is interesting to search for new half-Heusler compounds and study their physical properties. In this sense, we will discuss the substitution approaches that lead to the half-Heusler FTS materials and the design of new half-Heusler functional materials.

2. Substitution approaches of materials design

The substitution approach of materials design that derives a new materials family from a previously known parent materials family by partially substituting the elements in the chemical formula is an efficient rational approach for designing new compounds. The physical properties of the new materials are closely related to their parent materials systems, as the local structural motifs are to some extent maintained during the substitution process. Numerous physically interesting and technologically critical functional materials (*e.g.*, in Refs. [2], [4], [9]–[11]) have been designed via different types of substitution approaches.

The most straightforward substitution is to substitute part of the elements by the elements from the same group in the periodic table (*i.e.*, iso-group substitution), which could be applied to the wide-gap semiconductor cubic SiC[43] that can be derived from Si by substituting half of the Si atoms by C, specifically replacing all the Si atoms on one of the two fcc sub-lattices in the diamond structure. However, applying the iso-group substitution to other materials systems such as III–V and II–VI semiconductor alloys, in which one of fcc sub-lattices in the diamond-like structure is occupied by two types of elements, results in thermodynamically metastable phases[44–53] due to the strain energy arising from size-mismatch between the constituents. Note that the same atomic substitution in cubic SiC does not apply to the Si–Ge system since, chemically, Si and C are rather different thus gaining large chemical energy, whereas Si and Ge are quite similar. Therefore, the number of thermodynamically stable compounds derived from iso-group substitution is rather limited. In contrast, simultaneous substitution using multiple types of elements from different groups in the periodic table has been successfully applied for predicting new stable compounds in their simplest form with two types of substituting elements[9] called co-substitution.

2.1. Co-substitution

In the co-substitution approach,[9] a new compound is derived from the parent compound by replacing one type of elements by pairs of elements from other groups in the Periodic Table while keeping the number of valence electrons per atom unchanged (*e.g.*, replacing Zn by Cu and In). The mechanism for stabilizing a compound in co-substitution is analogous to the co-doping[54–56] physics involving pairs of donor and acceptor defects. The electrons transferring from donor to acceptor levels, and the donor-acceptor electrostatic attraction along with the atomic relaxations upon donor–acceptor pairing, are the main factors that stabilize the co-doping system. Co-substitution can be viewed as a 100% co-doping. In addition to the above energy saving factors, the ordering energy gained by forming ordered pattern in 100% co-doping that reduces strain energy, further stabilizes the co-substitution system. Co-substitution has been widely used in experimental and theoretical studies, leading to the discovery of many new stable compounds.[11,57–63] Several mutated types of co-substitutions were also used in materials design, *e.g.*, co-substitution with ordered vacancies[10,18,64–67] and co-substitution with filled interstitials.[17,19,68–74]

2.2. Substitution along with ordered vacancies

The substitution along with the formation of ordered vacancies in diamond-like structures was discussed in 1960 as a super-cell structure of semiconductors[10] with

$$\frac{\sum_i n_i v_i}{\sum_i n_i} = 4, \tag{1}$$

where n_i is the number of atoms of the ith kind (vacancies are considered as a kind of atoms) and v_i is its number of valence electrons. In this type of co-substitution one of the substituents was assigned to have zero valence electron and is represented by a vacancy. The stability of ordered vacancy compounds is well understood from defect physics, as clearly demonstrated in Refs. [64] and [65] for $CuInSe_2$, showing that the cluster of two Cu vacancies plus one In on Cu defect can have a large energy gain (3.45 eV) of clustering, much larger than the formation energies of individual defects. Therefore, a series of Cu–In–Se compounds, $Cu_{(n-3m)}In_{(n+m)}Se_{2n}$ ($m = 1, 2, 3, \ldots$; $n = 3, 4, 5, \ldots$), can form with different amounts of such defect clusters in $CuInSe_2$, such as $CuIn_3Se_5$, $CuIn_5Se_8$, $Cu_2In_4Se_7$, *etc*. It is not surprising from the chemical formulae point of view for the existence of these compounds, since their formulae are all combinations of Cu_2Se and In_2Se_3. However, it is surprising and interesting that they all have $CuInSe_2$-like structures with ordered defect clusters. It is also calibrated theoretically that, by forming ordered patterns, the ordered defec-

tive compounds gain an ordering energy of about 0.8 eV per cluster in the Cu–In–Se system.[64]

According to Eq. (1), the vacancy also has four valence electrons assigned to it in the diamond-like structures, which contribute to the formation of lone pair electrons of the four nearby anions pointing towards the vacancy as illustrated in the ordered vacancy compound $CdIn_2Se_4$[66] that can be derived from CdSe by forming defect cluster of one Cd vacancy plus two In on Cd defects per four CdSe formulae. Other ordered vacancy compounds such as Ga_2Se_3[67] (one Cd vacancy plus two Ga on Cd defects in 3 CdSe) and Sc_2S_3[18] (one Ca vacancy plus two Sc on Ca defects in 3 CaS) were also studied previously.

2.3. Substitution along with filled interstitials

There are plenty of crystal structures in nature that can be derived from other structures by filling some of their interstitial sites.[68–74] Filling the interstitial sites in semiconductors usually leads to metallic phases, as the interstitial defects are usually donors. If combining acceptor-like substitutions (*e.g.*, Sn on Sb) with filled interstitials to compensate the variation of valence electrons, one can design semiconductors stabilized by electron count even in complicated structures, such as the $LaCo_4Sb_9Sn_3$ filled Skutterudite semiconductor derived from the $CoSb_3$ Skutterudite semiconductor by filling La with three valence electrons on the interstitial site and substituting three Sb by three Sn atoms losing three valence electrons.[69]

The co-substitution approach along with filled interstitials has been extensively applied to diamond-like structures, leading to the discovery of many semiconducting compounds.[71–74] The diamond structure is one of most loosely packed three-dimensionally bonded structures in nature. In the unit cell of diamond structure, there are four fcc sub-lattices (see Fig. 1) and two of them are filled by atoms with the other two being empty; filling one of the empty fcc sub-lattice leads to the filled tetrahedral structure[17] also called half-Heusler structure (filling the two empty fcc sublattice leads to Heusler structure). This type of filled interstitial semiconductors was first discovered by Nowotny *et al.*[72] and Juza *et al.*[71] It is found that the filled interstitial could help to move some electronic states away from the band edges leading to direct band gaps, such as for indirect gap GaP, filling Li at the interstitial site and substituting Ga by Zn for valence electron compensation leading to a direct-gap semiconductor LiZnP.[17] Theoretical calculations[19] show that the filled interstitial structure has both strongly ionic bonds between anion and the interstitial (such as P–Li) and strongly covalent bonds between anion and the substituted cation (such P–Zn). Analogous to ordered vacancy compounds, filled interstitial compounds can appear in different stoichiometry's depending on the concentration of interstitial-substitution defect complexes. For example, there are ABX-type (*e.g.*, LiZnP),[17] A_3BX_2-type (*e.g.*, Li_3AlN_2),[74] and A_3X-type (*e.g.*, Li_3Sb)[73] filled interstitial structures derived from diamond-like structure with eight valence electrons per anion. Note that the A_3X-type filled interstitial structures have a Heusler-like structure.[73]

The half-Heusler compounds (*e.g.*, LiZnSb) can be derived from the Heusler-like A_3X-type compounds (*e.g.*, Li_3Sb) by co-substitution with ordered vacancies (*e.g.*, substituting one Li by Zn and removing another Li), which can also be viewed as filled interstitial structures derived from zinc blende compounds as discussed above. In the next section, we will discuss the focusing study of new half-Heusler compounds.

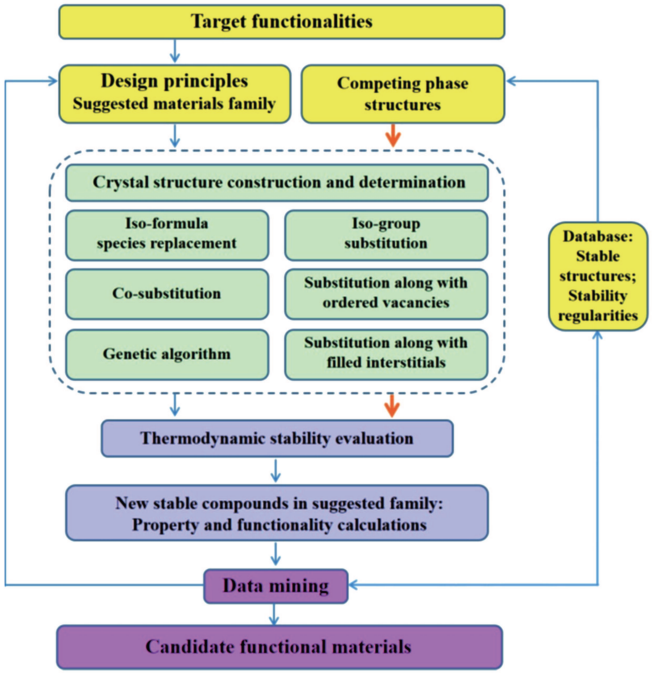


Fig. 2. (color online) Schematic diagram for the high throughput prediction of functional materials.

3. High-throughput prediction of new multifunctional half-Heusler materials

New half-Heusler ABX compounds can be derived from the existing Heusler materials or zinc blende compounds by introducing ordered defects (vacancies or interstitials), as discussed above; they can also be derived from the previously known half-Heuslers simply via iso-formula species replacement (*e.g.*, from LiZnN to NaZnN). However, one needs to check (i) whether the derived nominal compounds have the cubic half-Heusler structure, *i.e.*, structural determination; and (ii) whether they are thermodynamically stable against disproportionation into competing phases, *i.e.*, thermodynamic stability analysis, which are the main questions we are facing when predicting new multinary materials. Once the new compounds are predicted, theoretical evaluations of their physical

properties and functionalities could be performed to suggest candidate multifunctional materials. Figure 2 illustrates the process of high-throughput prediction of functional materials.

3.1. Structural determination

Prediction of the lowest-energy structure of a multinary compound can be solved successfully based on, *e.g.*, the global space group optimization (GSGO) method[75] that starts from randomly selected lattice vectors and random atomic positions within a cell as input for a sequence of *ab initio* calculations of total energy of locally relaxed trial structures to search for a global minimum via an genetic-algorithm selection. The GSGO method is successfully applied in predicting the lowest-energy structures of *ABX* compounds (*e.g.*, NaBaAs[76]). Analogous methods including simulated annealing,[77] evolutionary algorithm,[78,79] random search,[80] and particle-swarm optimization,[81] are also successful for a number of focused cases of structure prediction.[78–81] However, these coordination-based optimization methods[75,78–81] typically require significant computational resources to solve the lowest-energy structure of a single compound and is not tractable for high-throughput predictions of new materials.

Alternatively, one can use prior knowledge of the crystal structures of the existing compounds by constructing a tensor $T(c_i, e_j)$[82,83] for the known structures of given compositions (c_i) and sets of elemental constituents (e_j). $T(c_i, e_j) =$ "null" if for the composition c_i, *e.g.*, *ABX*, and the set of elemental constituents e_j, *e.g.*, NaZnN, the compound has not been reported yet. One can then construct a probability density $P(T(c_i, e_j))$ based on the tensor $T(c_i, e_j)$, considering (i) compounds in the same composition c_i (*e.g.*, NaZnN derived from LiZnN, NaZnP, NaZnAs, or NaZnSb, each derivation suggesting a structure), and (ii) compounds that the composition c_i can be derived from using *e.g.*, the substitution approaches discussed in Section 2 (*e.g.*, LiMgSb derived from GaSb based on co-substitution with filled interstitials). The probability density $P(T(c_i, e_j))$ can be used to suggest the possible crystal structures of unknown compounds. This methodology has been successfully applied in predicting the lowest-energy structures of a few hundred of new *ABX* compounds,[76,84] finding dozens of cubic half-Heusler structures as well as hundreds of non-cubic structures.

3.2. Thermodynamic stability analysis

The next step after structural determination for predicting the new compound is the evaluation of its stability relative to its competing phases by comparing their total energies or formation enthalpies. However, the standard approximations to density functional theory (DFT),[85,86] namely, the local density approximation (LDA)[87,88] or the generalized gradient approximation (GGA)[89] have to some extent numeric errors for predicting compounds' formation enthalpies, especially when the compounds and their competing phases belong to different chemical classes (*e.g.*, metal or non-metal). In Ref. [90], a computationally inexpensive theoretical approach based on GGA+U calculations with fitted elemental-phase reference energies (FEREs) that can be used for accurate predictions of the ΔH_f values of binary and multinary solid compounds involving chemical bonding between metals and nonmetals (such as pnictides, chalcogenides, halides). A set of FERE values[90] were obtained using an extensive set of 252 binary compounds with measured heat of formations, showing that the 252 formation enthalpies can be reproduced with the mean absolute error of 0.054 eV/atom after fitting instead of 0.250 eV/atom before fitting (see Fig. 3). Therefore, by providing accurate ΔH_f, the FERE approach[90] can be applied for accurate predictions of the compound thermodynamic stability with respect to decomposition into the competing phases.

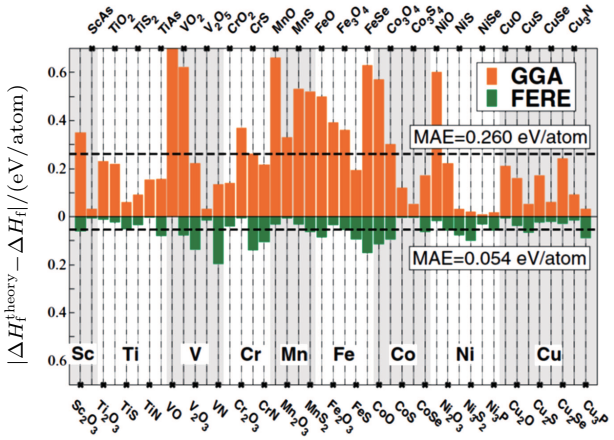


Fig. 3. (color online) Histogram showing absolute errors of the GGA (upper part) and of the FERE approach (lower part) in reproducing measured enthalpies of formation for 45 binary pnictides and chalcogenides containing 3d transition metals. Dashed lines represent the mean absolute error of the two methods corresponding to the full set of 252 binary compounds (Figure adapted from Ref. [90]).

In Refs. [76] and [84] on the prediction of new *ABX* half-Heusler compounds, the thermodynamic stability analysis is performed in the elemental chemical potentials space using the information of compounds' formation enthalpies (ΔH_f). A new compound (*e.g.*, *ABX*) is considered stable under the thermodynamic equilibrium conditions if there are values of the elemental chemical potentials (*e.g.*, $\Delta\mu_I$, $I = A, B, X$) that do not favor the formation of elemental (thus $\Delta\mu_I < 0$, $I = A, B, X$), binary (*e.g.*, A_lB_m thus $l\Delta\mu A + m\Delta\mu_B < \Delta H_f(A_lB_m)$), ternary (*e.g.*, $A_lB_mX_n$ thus $l\Delta\mu A + m\Delta\mu_B + n\Delta\mu X < \Delta H_f(A_lB_mXn)$) competing phases, but favor the formation of the target compound under thermodynamic equilibrium condition (*e.g.*, for *ABX*, $\Delta\mu_A + \Delta\mu B + \Delta\mu_X = \Delta H_f(ABX)$). The area in the elemental chemical potentials space that includes all the $\Delta\mu I$ values favoring the target compound but not competing phases can then be identified as the stability region. Figure 4 shows the calculated stability regions (in yellow)[91] of a few recently predicted *ABX* compounds.[84]

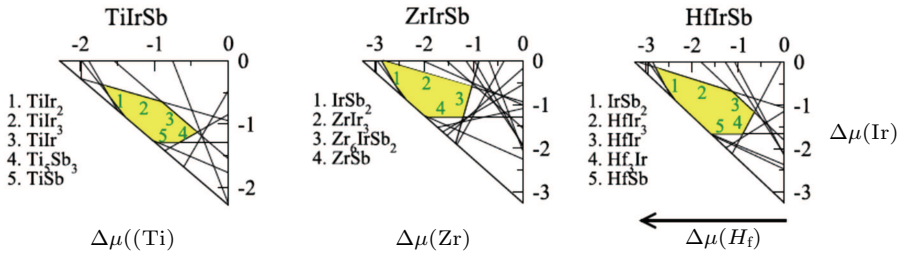


Fig. 4. (color online) The allowed chemical potential regions (yellow) in the chemical potential space of three cubic semiconducting *ABX* compounds, indicating also some of the phases competing with the stability of the *ABX* structure (Figure adapted from Ref. [91]).

3.3. Predicted *ABX* compounds and their functionalities

Following the above two steps of materials prediction (structure determination and thermodynamic stability analysis), 235 new *ABX* compounds with eight valence electrons (*e.g.*, LiMgSb)[76] and 54 new *ABX* with 18 valence electrons (*e.g.*, TaIrGe, see Fig. 5)[84] were predicted to be thermodynamically stable in their predicted lowest-energy structures. The compounds that already existed in ICSD[92] were in indicated by check marks in Fig. 5 and analogous figures in Refs. [76] and [84], The chemical trends concerning the appearance of cubic half-Heusler structure versus non-cubic structures as lowest-energy structures for each new or previously known *ABX* compounds were analyzed based on chemical bonding and elemental identity, suggesting that the half-Heusler structure is preferred mainly for compounds with covalent bonding features.[84] Dozens of the predicted *ABX* compounds[76,84] were realized in experiments,[32,35,84,93,94] confirming the theoretically predicted crystal structures and materials stability. Interesting physical properties and functionalities have been found in the new *ABX* compounds as discussed below.

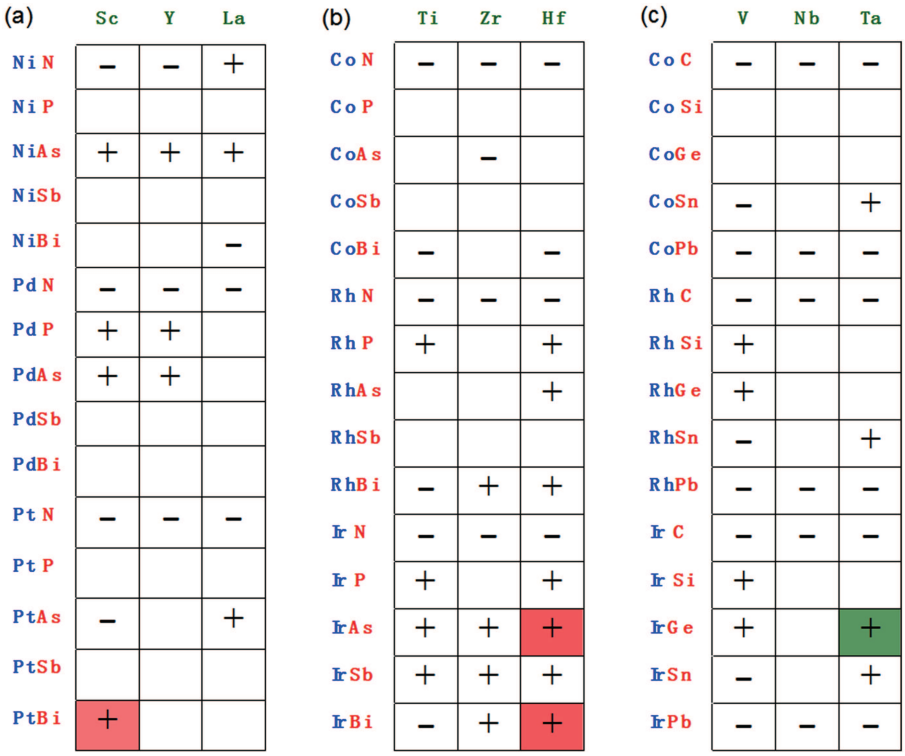


Fig. 5. (color online) *ABX* compounds with 18-valence electrons. Elements *A* are in green, *B* in blue and *X* in red. Check mark, previously reported compounds; plus sign, unreported and predicted here to be stable; minus sign, unreported and predicted here to be unstable. Green background indicates the predicted p-type transparent conductor; red background indicates the predicted topological semimetals.[84]

3.3.1. Topological semimetals

A number of *ABX* half-Heusler materials were found to be topological semimetals[26–29] analogous to HgTe including ScPtBi (with 18 valence electrons) that was a hypothetical half-Heusler structure considered in Ref. [26]. It is confirmed in Ref. [84] that ScPtBi is indeed thermodynamically stable with a cubic half-Heusler structure. Furthermore, two new topological semimetals (HfIrAs and HfIrBi) were predicted in Ref. [84] (see Fig. 6). The interesting trend in the HfIr(As, Sb, Bi) group of compounds with HfIrAs and HfIrBi being topological semimetal while HfIrSb in the middle being normal insulator[84] is related to the relatively high position of

the Sb-6s atomic level compared to the As-5s level and Bi-7s level.

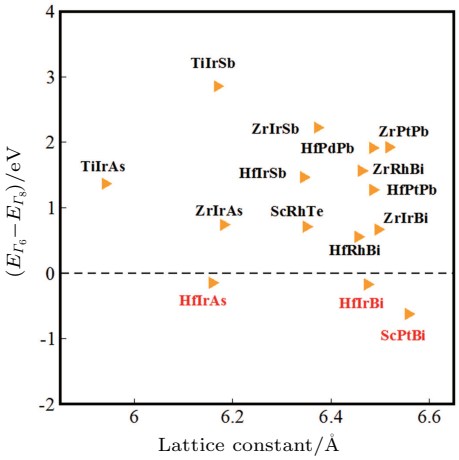


Fig. 6. (color online) Topological band characters of predicted *ABX* semiconductors and semimetals (Figure adapted from Ref. [84]).

3.3.2. Optoelectronic properties

The spectroscopic limited maximum efficiency (SLME)[95] for photovoltaic (PV) applications of the predicted new *ABX* compounds[76] were calculated based on GW approximation for the electron's self-energy.[96] Dozens of high SLME (> 20%) thin-film (500 nm) solar cell absorber materials (*e.g.*, CuCaN, CuNaS, NaMgBi, KYPb, *etc.*) were predicted.[76]

3.3.3. Thermoelectric properties

The existing 18-electron *ABX* compounds and their alloys are widely used in thermoelectric devices.[21–25]

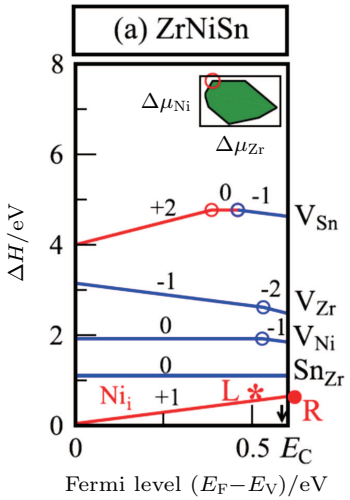


Fig. 7. (color online) Formation energy of the dominant defects versus parametric Fermi level in ZrNiSn from hybrid functional calculations. Main panel: positively charged electron–donor defects shown in red and negatively charged electron–acceptor defects shown in blue; their charge states denoted in numbers and their charge transition levels shown in open circles. The Fermi level, VBM and CBM variables are denoted by E_F, E_V, and E_C, respectively. The inset shows the allowed chemical stability region, whereas the red circle shows the specific chemical condition used for the current formation energy versus E_F calculations. The small vertical arrows indicate the position of the equilibrium Fermi level at growth condition of 850 °C (Figure adapted from Ref. [91]).

Many of the predicted *ABX* compounds could be candidate thermoelectric materials, *e.g.*, high thermopower (-153.9 mV·K^{-1}) and power factor (5.2 μW·cm^{-1}·K^{-2}) was found for the predicted and experimentally confirmed compound ZrNiPb,[84] whose neighboring compound ZrNiSn has already been widely studied for thermoelectric applications[21–25] (Figure 7 shows the calculated defect properties of ZrNiSn[91]).

3.3.4. Transparent conductor

A number of candidate transparent conductors were identified via materials design in the 18-electron *ABX* family.[32] These 18-electron *ABX* (*e.g.*, ZrIrSb, TaIrGe, and TaIrSn) are formed by heavy metals, whereas have wide band gaps induced by strong hybridization between the d orbitals of the two transition metals (*e.g.*, Ta and Ir).[32] Focusing our study on TaIrGe suggests that it is a transparent material with predicted low-concentration of intrinsic p-type carriers induced by the Ge on Ta anti-site defects, thus a potential p-type transparent conductor.[32] Furthermore, it is found that the valence band maximum state of TaIrGe is an anti-bonding state and is delocalized along the empty interstitial channels (in between the Ta–Ir and the Ta–Ge atoms), avoiding the ionic sites that consequently have but a low probability to scatter the mobile carriers. Subsequent experimental study confirmed the theoretically predicted crystal structure, optical transparency and low concentration of holes, thus the p-type transparent conductor functionality in TaIrGe. Significantly, it is discovered in experiments that TaIrGe has very high room temperature (RT) hole mobility (2730 cm^2·V^{-1}·s^{-1}),[32] higher than the previously reported RT hole mobility of Ge (1900 cm^2·V^{-1}·s^{-1}).[97]

3.3.5. Flexible three-dimensional inorganic semiconductors

In the MgSrSi-type crystal structure (*Pnma*), there are one-dimensional (1D) Mg–Si ribbons embedded in the three-dimensional (3D) matrix of Sr.

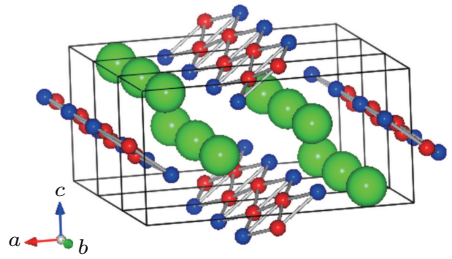


Fig. 8. (color online) Crystal structure of RbCuTe[35] in the MgSrSi-type structure. Green sphere: Rb. Red sphere: Cu. Blue sphere: Te.

Figure 8 shows the predicted MgSrSi-type structure of RbCuTe with a semiconducting band gap suitable for PV absorbers,[76] illustrating clearly the 1D Cu–Te ribbons in the 3D Rb matrix, which was confirmed in subsequent synthesis

and structure characterization.[35] RbCuTe was then found to be a flexible 3D inorganic semiconductor that can tolerant up to 30% strain with impunity due to the concerted rotation of the 1D Cu–Te ribbons in the inter-dimensional hybrid structure (IDHS). Theoretical design of this type of IDHSs in 3D inorganic compounds could suggest novel materials and new techniques for the flexible electronics technology.

4. Summary

Theoretical design of stable multinary functional materials could lead to the finding of interesting physical properties as well as technologically critical materials. We reviewed the rational substitution approaches for the design of multinary compounds and the high-throughput prediction of new multinary compounds, with their applications in the most succinct multinary family of *ABX* half-Heusler materials. The new functionalities of the predicted *ABX* materials were also discussed briefly. Many of the new *ABX* compounds were realized in experiments that confirmed the predicted crystal structures and physical properties.

The prediction of stable compounds at zero temperature is much faster and more straightforward than the anticipation of high-T phases. However, high-T phases, especially the RT structures, if different than the 0-K phases, are much more important than the latter for both technological application and scientific study. The methodologies and computational techniques for predicting material structures that are stable at nonzero temperature with comparable speed and confidence as the prediction of 0-K phases are crucial for the future high-throughput study of realistic functional materials for near-RT applications.

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