Prediction of A_2B $_4$ metal-chalcogenide compounds via first-principles thermodynamics

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Current compilations of previously documented inorganic compounds reveal a significant number of materials that are not listed. Focusing on the A_2BX_4 metal-chalcogenide group with A and B atoms being either main group elements or only one of them being a $3d$ transition metal, ation d,(atio)-380 TD3301.2(bne)-25/(,(a l3j*301.2(bne)u25 TJT*[(of)-38

130 000 inorganic substances with completely identified crystal structures and (2) the a —ICDD PDF[9]—that lists 300 000 x-ray diffraction data sets, we find that an additional 3000 A_2BX_4 members can be written down formally but are not reported. One wonders then how many unreported compounds are intrinsically (ther-modynamically) unstable, and how many exist but have yet to be explored, with potentially game-changing material functionality.

Along with high-throughput electronic band structure calculations for ICSD-existing materials,[10] knowledge-driven high-throughput computational techniques based on data mining[11,12] have been used to predict 200 new oxide ternary compounds.[13] On the other hand, quantum calculations of unknown materials without assessing their thermodynamic stability[14–16] continue to suggest promising physical properties in potentially unstable materials. One might suspect that certain metastable structures are kinetically sufficiently protected against thermodynamic instabilities to have usefully long lifetimes including nearly all semiconductor superlattices grown from the gas phase[17–19] or nitrogen dissolved in ZnO from a high-energy nitrous oxide source,[20] all corresponding to thermodynamically positive formation enthalpies. How-ever, it is possible that many hypothetically conceived 3D inorganic structures might, in fact, be readily decomposable into their various constituents. Indeed, quantum predictions of interesting physical properties in hypothetical 3D inorganic materials and structures without assessing their thermody-namic stability[14–16] might correspond to structures that are insufficiently protected by kinetic barriers, preventing perhaps at the outset even their synthesis.

Here, we focus on just a subset of the A_2BX_4 compounds: those with A and B atoms being either main group elements or only one of them being a $3d$ transition metal. Specifically, two groups of such missing A_2BX_4 materials for each $X =$ O,

FIG. 1. (Color online) A_2BX_4 (X = O, S, Se, Te) compounds in this study. The compounds labeled by plus, minus, and circle signs are unreported (UR) in ICSD and ICDD PDF.

S, Se, and Te can be constructed. In Fig. 1 we indicate those compounds that have been reported in the literature with a check mark, whereas all entries in Fig. 1 that are listed with a symbol (see legend) that includes "UR" are currently unreported. The groups considered are: (1) III_2-II-VI_4, III = Al, Ga, In, II = Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg, Sn, $3d$ elements except Sc; or III = 3

binary and/or ternary compounds. The list of yet undiscovered 100 metal chalcogenides is interesting because (i) they display fascinating chemical trends from oxides to tellurides, (ii) some of them contain elements in their rare oxidation states (e.g., Ti^{3+}) or uncommon coordinations, and (iii) dozens of them are not hard to synthesize in terms of growth condition, as estimated from first-principles calculations.

II. APPROACH FOR DETECTING OVERLOOKED $A_2B\quad_4$ COMPOUNDS

Figure 2 illustrates some of the b̌   ̌   required to predict the existence of multinary compounds. One faces two main problems. Firstly, there is a question of the lowest-energy crystal structure of an unknown ternary compound. This is a complex problem as there are, in principle, infinitely many possibilities. Second is the question of the stability of a given compound with respect to decomposition into its competing phases, such as either pure A, B, and X elements, or combinations of the pure elements with other binary and/or ternary compounds within the same A-B-X chemical system. In this section we describe our approach to solving these two problems.

A. Determination of the structure type of a specific ternary $A_2B\quad_4$ compound

The problem of the lowest-energy crystal structure of a multinary compound can be solved successfully by applying the global space group optimization (GSGO) method.[21] The input of the GSGO method consists of random lattice vectors and random Wyckoff atomic positions, so the structure is unbiased. It then uses a real-space genetic-algorithm selection of structures, involving structure mating and mutation. The approach uses a sequence of *ab*   density functional evaluation of total energies of locally relaxed trial structures so as to seek the lowest-energy structure. Such GSGO typically requires significant computational resources to solve the low-energy structure problem for a single set of A, B, and X elements. It is not tractable within high-throughput approaches that aim at predicting a large number of missing/potentially overlooked compounds.

Alternatively, one can construct a set of likely candidate crystal structure types for A_2BX_4 and compute their total energies subject to local relaxation, then select the lowest-energy structure from this list. The list of candidate structure types is created from those which are known from existing A_2BX_4 compounds. It has been shown in Ref. 6 that   800 reported A_2BX_4 compounds crystallize in 32 different structure types. Out of 32 we exclude four since each of them represents only one reported A_2BX_4 compound containing either Li or H. We enrich the set of structure types by recognizing an important structural feature of ternary materials, the possibility that the A and B atoms exchange their lattice sites. For example, spinels are known to exist in the normal spinel structure, where the A atoms are octahedrally coordinated and the B atoms are tetrahedrally coordinated (as in Al_2MgO_4), and in the inverse spinel structure which is equivalent to a 50%-50% alloy of A and B atoms over the octahedral sites (such as Mg_2TiO_4[22]). By reviewing the ICSD .l247 91.6501 Tm[(),)-263.1(and)s4(he)[(sp)-2ning26.4ie coordina.8(er755.6(x TD8(er76-316)]TJ6ele0.7(a)70.7(a)
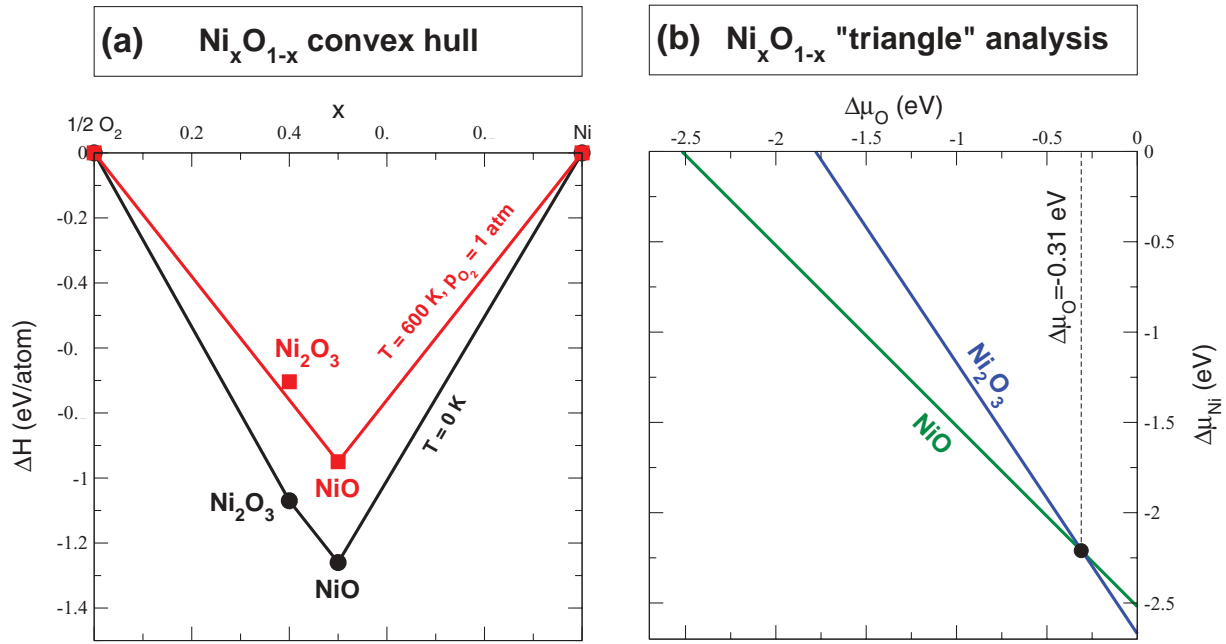
FIG. 3. (Color online) (a) Ground-state lines of Ni O$_{1-}$ system for T = 0 (black line) and 600 K (red/gray line). (b) Chemical potential diagram of Ni O$_{1-}$ system.

hull) as shown in Fig. 3(a) for the Ni O$_{1-}$ system. At each fixed composition (canonical ensemble), the compound on the ground-state line, e.g., NiO with 50 : 50 composition, has lower energy than any linear combination of other compounds in this system that sum up to the examined composition (e.g., NiO). Therefore the compounds on ground-state line are all stable with respect to disproportionation into their competing phases. The con werwba042 gctwba0429(c7042 gct).9(c 11.703(os(738 058o611.70s15.7(xamined(aro611.70s(as)]o[(system))-2 Tj/FectNx

TABLE IV. List of unreported A_2BX_4 selenides predicted to be stable (28 compounds in total). Predicted structure, the ΔH_f value (in eV/atom), Δ_{Se}^{min}, and Δ_{Se}^{max} (in eV) are presented.

A_2BX_4	Structure type	ΔH_f	$\Delta_{Se}^{min}/\Delta_{Se}^{max}$	A_2BX_4	Structure	ΔH_f	$\Delta_{Se}^{min}/\Delta_{Se}^{max}$
Al_2BeSe_4	b4I	−1.06	−1.84/0.0	In_2NiSe_4	b5I	−0.54	−0.33/0.0
Al_2CoSe_4	b4	−0.91	−0.92/0.0	In_2SnSe_4	b10I	−0.60	−0.36/0.0
Al_2FeSe_4	b4I	−0.94	−1.07/0.0	In_2VSe_4	b5I	−0.78	−0.53/0.0
Al_2TiSe_4	b10I	−1.14	−1.88/−1.24	Sc_2BaSe_4	b9	−2.04	−2.86/0.0
Al_2VSe_4	b10I	−1.11	−1.87/0.0	Sc_2SrSe_4	b9	−2.02	−2.75/0.0
Co_2SiSe_4	b4I	−0.45	−0.56/−0.08	Sr_2SiSe_4	b10	−1.55	−0.85/0.0
Co_2SnSe_4	b4	−0.36	−0.43/−0.14	Ti_2BaSe_4	b34	−1.56	−1.45/−0.54
Cr_2BaSe_4[a]	S2I	−1.17	−0.35/0.0	Ti_2BeSe_4	b7	−1.15	−0.92/−0.70
Cr_2MgSe_4	b6	−0.96	−0.76/0.0	Ti_2CaSe_4	d3	−1.50	−0.89/−0.72
Fe_2SiSe_4	b10	−0.49	−0.78/0.0	Ti_2CdSe_4	b7	−1.12	−1.25/−0.60
Ga_2BeSe_4	b4I	−0.85	−0.55/0.0	Ti_2HgSe_4	b37	−1.00	−0.87/−0.40
Ga_2CoSe_4	b4	−0.71	−0.72/0.0	Ti_2MgSe_4	b6	−1.33	−1.39/−0.56
In_2BeSe_4	b4I	−0.74	−0.52/0.0	Ti_2SrSe_4	b9	−1.55	−1.13/−0.66
In_2CrSe_4	b5I	−0.68	−0.31/0.0	Ti_2ZnSe_4	b7	−1.16	−1.46/−0.54

[a]This compound is neither in ICSD nor in ICDD PDF but can be found in Ref. 47.

higher-energy structures of the 100 stable A_2BX_4 compounds are given in Appendix A.

Some of the predicted compounds contain elements in uncommon coordinations, e.g., (i) Mg surrounded by O_4 tetrahedron (instead of normal O_6 octahedron) in Ni_2MgO_4, (ii) Cd surrounded by O_4 tetrahedron (instead of normal O_6 octahedron) in Ni_2CdO_4 and Co_2CdO_4, (iii) Ca surrounded by S_8 c[((ii))-of t in Ni

B. Comparison with previous work on new oxides

A high-throughput computational technique have been applied to predict 209 oxide ternary compounds,[13] using the data mining based model to suggest the composition (e.g., A B O

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