

SUPPLEMENTARY DATA:

Realization of predicted exotic materials: The burden of proof

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Supplementary S1: Methods

All first-principles calculations are carried out using the Vienna Ab Initio Simulation Package (VASP)[1-3] using Perdew-Burke-Ernzerhof (PBE) functional[4]. For InN and InAs systems, we also performed calculations using Heyd-Scuseria-Ernzerhof (HSE) screened hybrid functional[5]. Spin-orbital coupling is included in the analysis of electronic properties of InAs, InN, BiO₂, BaBiO₃, and Ba₄Bi₃. The calculations for electronic and magnetic properties of CuBi₂O₄ is performed at PBE+U level introduced by Dudarev *et al.*[6] U-J = 6 eV is used for d-like orbitals of Cu. The analysis of results is made using pymatgen[7] and Vesta[8].

Convex hull calculations: To calculate energy convex hull, we first form the dataset of all competing phases. **For the Bi-O system**, the dataset is formed via including all Bi-O structures available in Inorganic Crystal Structure Database (ICSD)[9], Materials Project[10], and Automatic Flow (AFLOW)[11] databases. We also include BiO₂ in the assumed β -cristobalite SiO₂ structure[12]. **For the Ba-Bi system**, the structure dataset includes all structures available in ICSD and Materials Project database. We use O₂ molecule as the reference state for calculations of oxygen chemical potential. Γ -centered Monkhorst-Pack k-grids[13] are used in the Brillouin-zone with the with grid density of approximately 10000 per reciprocal atom ($N_{kpt} \times N_{atoms} \approx 10000$). For each system, random atomic displacements within 0.1 Å are applied in order to avoid trap at a local minimum. Next, we compare the structure before structural perturbation with that after full relaxation of the perturbed system. If the structures are different, we also perform additional calculations for the unperturbed system. To describe the chemical potential for the reference state accurately, we implemented fitted elemental-phase reference energies (FERE) corrections[14].

Defect calculations: 112-atom supercell are used to calculate Bi defect energetics in Ba_4Bi_3 . The defect formation energies and finite size corrections are computed within the framework described by Lany and Zunger[15,16] and implemented in the pylada-defects code[17]. The ranges of chemical potentials are determined from convex hull calculations described above.

Band unfolding calculations: To study the effect of spontaneous formation of Bi vacancy on the electronic structure of Ba_4Bi_3 , we created the range of OVC's. Using 112-atom supercell, we identify the lowest energy arrangements of 1, 2, and 3 Bi vacancies via screening of all unique vacancy arrangements. For simplicity of band unfolding calculations, we assume that the formation of Bi vacancies does not change the lattice vectors. To calculate the effect of the concentration of Bi vacancies on the electronic structure of Ba_4Bi_3 , only the lowest energy vacancy arrangements were considered. The supercell (with defects) band structures were then unfolded into primitive Ba_4Bi_3 Brillouin zone using Effective Band Structure method[18,19] and a modified version of BandUP code[19].

Calculations of n-type doping in BaBiO_3 : To study the effect of n-type doping on band inversion in BaBiO_3 , we considered experimentally reported $\text{BaBiO}_{2.5}$ structure[20] and Li-doping of BaBiO_3 . To study Li-doping of BaBiO_3 , we perform screening of 42 unique arrangements of 4 Li atoms in the primitive cell of monoclinic BaBiO_3 (space group: 14). Finally, all obtained structures are checked with respect to random atomic displacements. To understand the effect of Li doping on the electronic structure of BaBiO_3 , only the lowest energy structure found from screening is used.

Phonon calculations: The normal modes are calculated with harmonic approximation using PHONOPY package[21-23] to construct and evaluate the dynamical matrix composed of DFT force constants. The finite displacement method[24] (i.e., supercell approach) was used to approach the force constants. Within a primitive cell of N atoms, there are $6N$ possible displacements $(\pm x, \pm y, \pm z)$, which can be reduced due to the crystal symmetry. For BiO_2 (SiO_2 -type) structure with 6 atoms and Fd-3m space group, the 36 possible displacements are reduced to 2 displacements. The phonon dispersion (for q points away from the Brillouin-zone center) is probed in a $2 \times 2 \times 2$ supercell.

Supplementary section S2: Finite temperature effects on the ground state structures of Bi-O

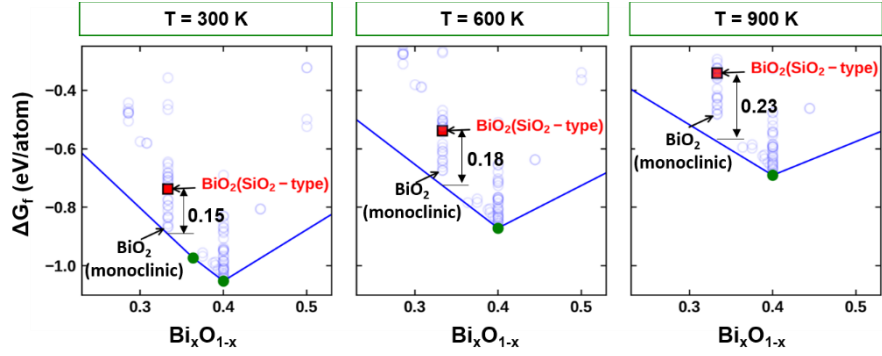


Figure S1. Convex hull of Bi-O system at $T = 300\text{-}900\text{ K}$ are predicted using machine learning model. The free energies of oxygen and bismuth refer to the experimental data[25]. The free energy $G(T)$ is obtained with respect to formation enthalpy by the following expression:[26]

The Gibbs free energy with respect to formation enthalpy at 0 K is:

$$G(T) = \Delta H_f(0K) + G^\delta(T), \quad (1)$$

where $\Delta H_f(0K)$ is the formation enthalpy at 0 K, as $G^\delta(T)$ is the energy that determined in the experiment and approximated using the following machine learning model:

$$G^\delta(T) = (-2.48 \times 10^{-4} \times \ln(V) - 9.94 \times 10^{-5} mV^{-1})T + 0.181 \times \ln(T) - 0.882 \quad (2)$$

where V is the volume per atom of the calculated structure, m is the reduced mass which is expressed as $\frac{1}{m} = \sum_{i=1}^N \frac{1}{m_i}$.

The formation free energy $\Delta G_f(T)$ is defined as follows:

$$\Delta G_f(T) = \Delta H_f(298K) + G^\delta(T) - \sum_{i=1}^N a_i G_{i,exp}(T), \quad (3)$$

where $G_{i,exp}(T)$ is the experimentally determined standard free energy of elements[25].

Supplementary section S3: Spontaneous formation of Bi vacancy in Ba_4Bi_3 resulting in the splitting of the Dirac cone in Ba_4Bi_3

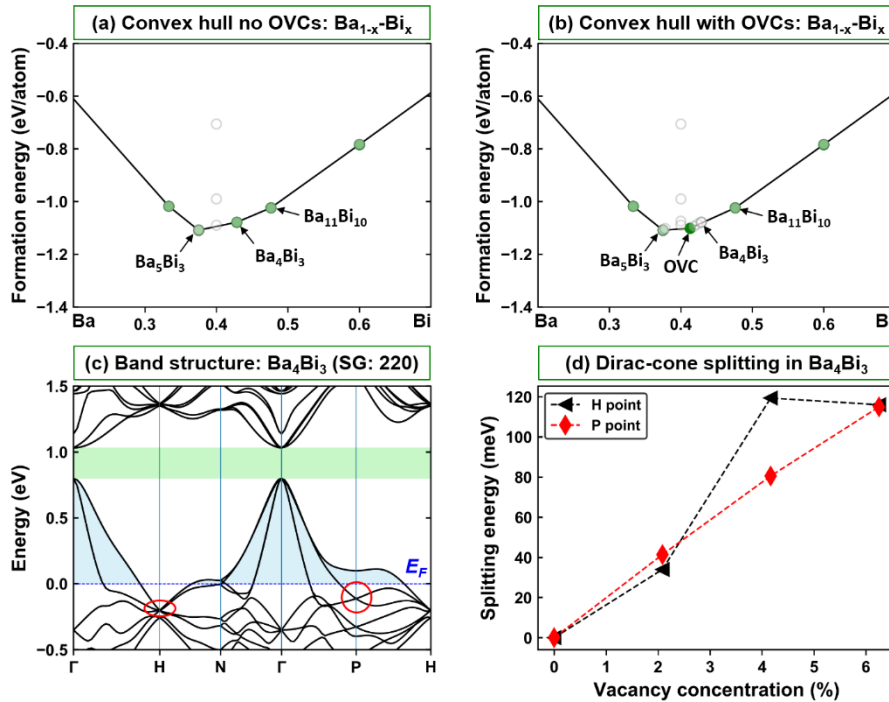


Figure S2. (a) Ba-Bi convex hull determined considering only known phases. Bi-rich and Bi-poor conditions for defect calculations presented in Fig. 2b are determined by competing of Ba_4Bi_3 with $\text{Ba}_{11}\text{Bi}_{10}$ and Ba_5Bi_3 phases, respectively. (b) Ba-Bi convex hull determined considering known phases and OVCs. The results show that OVC is the ground state. When Bi-deficient OVCs are included in convex hull calculations, Ba_4Bi_3 becomes above the convex hull. (d) Direct-cone splitting in Ba_4Bi_3 as a function of the concentration of Bi vacancies. The splitting energies in (d) are calculated as the energy difference among band branches that were degenerated in pristine structure but are split when Bi vacancies exist.

Supplementary section S4: Energy stabilization by various magnetic arrangements in CuBi_2O_4

CuBi_2O_4 was first studied in the 90's, when its crystal and magnetic structure were thoroughly described. Most of these studies report its structure to have the 130 space group (P4/ncc)[27]. This crystal structure contains parallel lines of Cu atoms. The existence of these lines impacts directly on its magnetic configuration. Both experimental (neutron diffraction)[28] and our theoretical results report that the AFM configuration is the most stable. Another crystal structure for this material with a different space group (I4cm, space group 108)[29] is found to be significantly less stable. In table SI, we report the energy difference among several of these structures, considering different spin configuration as: non-magnetic (NM), ferromagnetic (FM) and a few different arrangements of antiferromagnetic (AFM). We have also tested a paramagnetic configuration, where the spin orientations are distributed using the SQS (special quasirandom structure) approach using supercell with 756 atoms, similar to what was performed before for transition metal oxides[30].

Table SI: Relative total energies for different crystal structures (space groups) and magnetic configurations with respect to the most stable AFM configuration. FM refers to ferromagnetic, NM to non-magnetic, AFM to antiferromagnetic and PM to paramagnetic.

Space Group	Magnetic configuration	Relative total energy (meV/f.u.)
130	AFM1	0
130	AFM2	+1
130	PM	+3
130	AFM3	+6
130	FM	+7
130	NM	+498
108	AFM	+692
108	FM	+723

Supplementary section S5: n-type doping destroying excited state band inversion in BaBiO₃

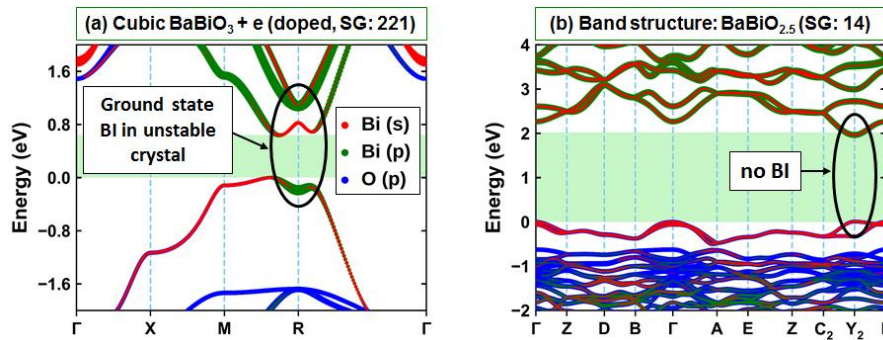


Figure S3. n-type doping destroying excited state band inversion in BaBiO₃. (a) The band structure of heavily electron-doped cubic BaBiO₃ where the target band inversion (BI) has now moved closer to the Fermi level. The cubic BaBiO₃ structure is unstable with respect to disproportionation of two of its BiO₆ octahedra into different (small vs. large) octahedra, giving the known stable monoclinic structure (space group 14) that also has excited state band inversion at about 2 eV above the Fermi level. This high energy band inversion is, however, unstable with respect to n-type doping where a normal band order (Bi, s in red below Bi, p in green) for (b) O-deficient sample is seen.

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