Defect-Enhanced Void Filling and Novel Filled Phases of Open-Structure Skutterudites

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Computational details

All the calculations are carried out in projector augmented wave (PAW) method, as implemented in the Vienna *ab initio* Simulation Package (VASP), and the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) for the exchange-correlation potential is used for all the calculations. Computational details are as in prior publications.[1-3] All calculations for pure and doped $CoSb_3$ skutterudites are carried out on a supercell (2×2×2 primitive cell) with a total of 128 atoms and 8 voids. A 3×3×3 Monkhorst-Pack uniform k-point sampling is used for energy calculations of supercell and 15×15×15 Monkhorst-Pack uniform k-point sampling is used for other compounds.[4] Lattice constants are optimized by fitting the Birch–Murnaghan equation of state.[5] and ion positions are relaxed until the Hellmann-Feynman forces acting on each atom is less than 10^{-2} eV/Å. Different atomic configurations are considered and the one that has the lowest energy is used for our calculations. Because all the calculations are carried out in supercells, and the doped fraction of Ga and In is small, their effect on the lattice parameter is small and can be effectively ignored in our study.

Table S1. Lattice constant of Ga/In doped $CoSb_3$ skutterudites.

The value of y	Lattice constant of $Co_4Sb_{12-y}Ga_y$(Å)	Lattice constant of $Co_4Sb_{12-y}In_y$(Å)
0	9.118	9.118
0.125	9.114	9.121
0.25	9.111	9.124
0.5	9.102	9.128

Table S2. Enhancement of the *FFL* (ΔFFL_C) of various filler atoms at charge compensated system with Ga/In in Sb sites.

Impurities Charge State	ΔFFL_C-Ga_{Sb}	ΔFFL_C-In_{Sb}
+1	0.44	0.14
+2	0.22	0.07
+3	0.147	0.047
+4	0.11	0.035

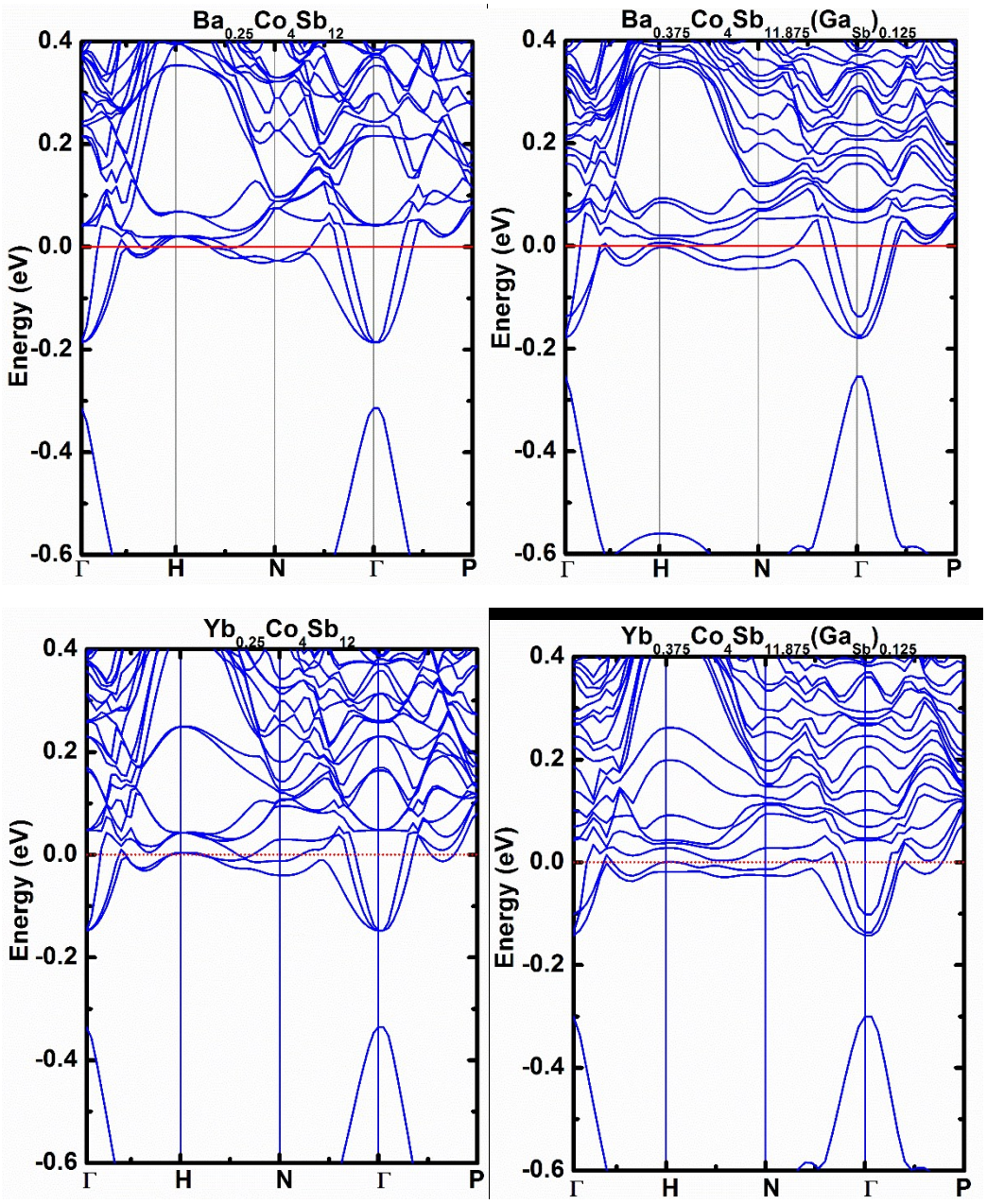

Figure. S1 Band structures of Ba-, Yb-filled skutterudites with and without charge compensation of Ga. The red lines indicate Fermi level.

$$yYb + Co_{32}Sb_{95}X \rightarrow Yb_yCo_{32}Sb_{95}X$$
$$\Delta H_1(y) = (E_{Yb_yCo_{32}Sb_{95}X} - E_{Co_{32}Sb_{95}X} - y\mu_{Yb})/y \quad \text{(S1)}$$

$$15Yb + Co_{32}Sb_{95}X \rightarrow 32CoSb_2 + 15YbSb_2 + XSb$$
$$\Delta H_2 = (32E_{CoSb_2} + 15E_{YbSb_2} + E_{XSb} - E_{Co_{32}Sb_{95}X} - 15\mu_{Yb})/15 \quad \text{(S2)}$$

Where $X = Ga, In$ represents the charge compensated impurities. $\Delta H_1(y)$ and ΔH_2 are the formation enthalpies of the filled skutterudites and of secondary phases, respectively. E_{ER} is the total energy of compounds *R*. μ_{Yb} is the chemical potential of the impurity Yb.

1 P. E. Blöchl, *Phys. Rev. B* **1994**, *50*, 17953; G. Kresse and J. Koubert, *ibid.* **1999,** *59*, 1758.

2 J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett*. **1996**, *77*, 3865.

3 G. Kresse and J. Furthmüller, *Phys. Rev. B.* **1996,** *54*, 11169; G. Kresse and J. Hafner, *ibid.* **1993,** *47*, 558.

4 The Birch–Murnaghan equation for the energy E as a function of volume *V* is $\mathrm{E(V)}=\mathrm{E_0}+\frac{9}{8}KV_0[(V_0/V)^{2/3}-1]^2[1+(4-K'/2)(1-(V_0/V)^{2/3})]$, where E and $\mathrm{E_0}$ are the energy and minimum energy, *V* and V_0 are the volume and volume at the minimum Energy, and *K* and K' are the bulk modulus and its pressure derivative.

5 H. J. Monkhorst, J. D. Pack, *Phys. Rev. B*. **1976**, *13*, 5188.