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## Novel ternary sulfide thermoelectric materials from high throughput transport and defect calculations: Supplementary Informations

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## **Defect Calculations**

In this section, we shall present the detailed defect calculations for all the five thermodynamically stable ternary sulfides (with  $\Delta E_{\text{hull}} = 0$ ), identified in this work.



FIG. 1. (top) The atomic chemical potential ranges ( $\Delta \mu_{\alpha}$  where  $\alpha$  is Ca, Sb and S) that would result in thermodynamically stable Ca<sub>2</sub>Sb<sub>2</sub>S<sub>5</sub> and exclude the formation of competing phases are illustrated. The defect energies are evaluated at the three highlighted points. (bottom)  $E_D$  vs  $\mu_e$  for the intrinsic defects are shown. Here, n-doping will be difficult due to stable Ca<sub>2</sub>b, hole producing killer defect.

We first start with discussing n-doping in Ca<sub>2</sub>Sb<sub>2</sub>S<sub>5</sub>. The atomic chemical potential ranges  $\Delta \mu_{\alpha}$  ( $\alpha$  is Ca, Sb and S) which results in thermodynamically stable host and prevents the formation of competing phases are shown in Fig. 1 (top), in grey. The formation energy of intrinsic defects as a function of electronic chemical potential,  $\mu_e$ , that spans within the bandgap of the host are shown in the bottom panel of Fig.1. These were calculated for three points corresponding to the boundaries of the  $\Delta \mu_{\alpha}$  values (Fig. 1, top). The most stable intrinsic defect is a negatively charged, hole producing Ca<sub>Sb</sub> antisite defect, for points 2 and 3. This Ca<sub>Sb</sub> is a compensating defect that would prevent n-doping in Ca<sub>2</sub>Sb<sub>2</sub>S<sub>5</sub>. Even for point 1, which is Ca poor (high negative  $\Delta \mu_{Ca}$ ), the Ca<sub>Sb</sub> is stable giving a  $\Delta \mu_D < -0.3$  eV thereby preventing *n*-doping.



FIG. 2. (top) The chemical potential ranges ( $\Delta \mu_{\alpha}$  where  $\alpha$  is Na, Sb and S) that would result in thermodynamically stable NaSbS<sub>2</sub> are shown. (bottom)  $E_D$  vs  $\mu_e$  for the intrinsic defects are depicted. Here *n*-doping will be impossible due to stable killer Na<sub>Sb</sub> defect, among other hole producing defects.

The next candidate is NaSbS<sub>2</sub>. In Fig. 2 (top and bottom), we present respectively the atomic chemical potential window,  $\Delta \mu_{\alpha}$  ( $\alpha =$ Na,Sb,S) that would result in stable host and the formation energies versus  $\mu_e$  plots for the corresponding intrinsic defects. We note that there is a stable killer defect, Na<sub>Sb</sub>, that would prevent *n*-doping of the host compound and would result in low carrier concentration. Unfortunately, the killer defects cannot be removed by going to any favourable  $\Delta \mu_{\alpha}$  values.

The next candidate is  $CuSbS_2$  and in the top and bottom panel of Fig. 3, we respectively show the chemical



FIG. 3. (top) The chemical potential ranges that would result in thermodynamically stable CuSbS<sub>2</sub> are shown. (bottom)  $E_D$  vs  $\mu_e$  for all the intrinsic defects are shown, which indicates a stable electron killer, Vac<sub>Cu</sub>.



FIG. 4. (top) The chemical potential ranges that would result in thermodynamically stable RhSbS. (bottom) Defect formation energies of the intrinsic defects in RhSbS. The large bandgap of the compound together with a stable  $S_{\rm Sb}$  anti-site defect would make it difficult to n-dope RhSbS.

## Energy correction to defect formation energy

Formation energy of a defect D with charge q has been defined previously [Eq. (2), main paper] as,

$$E_{D(q)}[\mu_e] = E_{f,D(q)} - \sum_{\alpha} n_{\alpha} \Delta \mu_{\alpha} + q \mu_e.$$
(1)

In the previous section, we have already discussed how the elemental chemical potentials,  $\Delta \mu_{\alpha}$  are relavant to the evaluation of  $E_{D(q)}$ , for all five candidates.

The formation energy of the defect with respect to the reference states of the defect forming atoms  $\alpha$  given as,

$$E_{f,D(q)} = E_{D(q)} - E_{\text{bulk}} - \sum n_{\alpha} E_{\alpha}.$$
 (2)

This is calculated using a super-cell approach. Evaluation of  $E_{\text{bulk}}$  and  $E_{\alpha}$  in Eq. (2) are straight forward. However, when estimating the energies of the charged defect  $E_{D(q)}$ , one needs the following corrections to the DFT energies,

$$\Delta E_{\rm corr} = \Delta E_{\rm VBM} + \Delta E_{\rm MP}(q) + \Delta E_{\rm PA}[D(q)].$$
(3)

The electronic chemical potential,  $\mu_e$ , is always measured with respect to the VBM of the pristine super-cell. In

potential window  $\Delta \mu_{\alpha}$  ( $\alpha$  is Cu,Sb,S) and the defect formation energies of its intrinsic defects. We observe that the most stable defect is Vac<sub>Cu</sub>. We observe that even at point 1, which is Cu richest ( $\Delta \mu_{Cu} = 0$ ), Vac<sub>Cu</sub> is low in energy. Since the hole producing, negatively charged Vac<sub>Cu</sub> defect is stable across all values of  $\Delta \mu_{\alpha}$ , it effectively rules out any chance of achieving n-doping.

The chemical potential window  $\Delta \mu_{\alpha}$  ( $\alpha$  is Rh,Sb,S) that would produce thermodynamically stable RhSbS is shown in top panel of Fig. 4. In the bottom panel, we illustrate the defect formation energies of all the intrinsic defects. We note that the S<sub>Sb</sub> anti-site defect (hole producing) is stable, and would prevent *n*-doping in the host.

The final candidate is CoSbS. The energy of formation of the different intrinsic defects within the bandgap are illustrated in Fig. 5. Note that the most stable intrinsic defects ( $S_{Sb}$  and  $Sb_{S}$ ), are relatively high in energy. Thus, the compound has no intrinsic compensating defects.



FIG. 5. (top) The chemical potential ranges that would result in thermodynamically stable CoSbS are shown. (bottom) The defect formation energies of the intrinsic defects of CoSbS are illustrated.  $S_{Sb}$  anti-site is the most stable compensating defect, but is high in energy and will therefore not affect n-dopability of the candidate.

the charged defect,  $\Delta E_{\text{VBM}}$  aligns the top of the valence band of the defected and non-defected cell. To remove the spurios effect of interaction between image charges in a finite super-cell, multipole corrections are implemented according to the method of Makov and Payne[1]. The correction  $\Delta E_{\text{MP}}(q)$  is given by,

$$\Delta E_{\rm MP}(q) = \frac{q^2 M}{2L\epsilon} + \mathcal{O}(L^{-3}), \qquad (4)$$

here M is the Madelung constant of the supercell Bravais lattice,  $\epsilon$  is the static di-electric constant, L is the distance between defect centers.  $\epsilon$  is obtained from VASP using Density Functional Perturbation Theory.[2].

The net charge of the super-cell is compensated by a constant background charge. In this case, the Kohn-Sham eigenvalues are only defined up to a constant, which in-turn depends on the average crystal potential. This potential in the defect containing super-cell and in bulk must be aligned [3, 4]. The total energies of the super-cells containing charged defects and the pristime bulk are corrected by,  $\Delta E_{\rm PA}[D(q)] = q[V_R(D(q)) - V_R^{\rm bulk}]$ . Here the term  $V_R(D(q)) - V_R^{\rm bulk}$  is the difference between the potentials at a reference point R, for the charged defect and the pristine (bulk) super-cell. Thus,

TABLE I. k-points corresponding to the electron pockets in Fig. 5 of main paper.

the premise of the correction is that, creation of a defect results in a constant shift in the potential  $V_R$ .

The defect calculations were performed on a  $3 \times 3 \times 3$  kmesh using the VASP code.[5] The super-cells sizes were chosen to contain a minimal number of atoms under the condition that the defects are separated by at least 10 Å. The super-cell for the candidates explored in this work contains 96 atoms for CoSbS, RhSbS and CuSbS<sub>2</sub>; 128 atoms for NaSbS<sub>2</sub> and 72 for Ca<sub>2</sub>Sb<sub>2</sub>S<sub>5</sub>. We found these super-cell sizes to be well converged.

To test the convergence with respect to supercell size we have performed calculation for larger cells of NaSbS<sub>2</sub> and CuSbS<sub>2</sub> in Fig. 6. We plot the energy of formation  $\Delta E_{D(q)}$  versus  $\mu_e$  (in Fig. 6) for the most stable defect, i.e. Na<sub>Sb</sub> for NaSbS<sub>2</sub> and Vac<sub>Cu</sub> for CuSbS<sub>2</sub>.

In the case of NaSbS<sub>2</sub>, the comparision is shown between a  $2 \times 2 \times 1$  super-cell containing 64 atoms versus a  $2 \times 2 \times 2$  super-cell containing 128 atoms. We notice that the differences in formation energy between the Na<sub>Sb</sub> defects are small. There are slight discrepancies but only in the order of a few meVs, near the Valence Band Maximum (VBM) and the Conduction Band Minimum (CBM). The discrepancies are due to which charged defect are stable (q or  $q \pm 1$  near the band extrema).

In the case of CuSbS<sub>2</sub> which is orthorhombic with a short *b* axis, we illustrate the results for  $2 \times 2 \times 1$  supercell containing 80 atoms versus a  $2 \times 3 \times 1$  super-cell containing 96 atoms. Again, in both cases the formation energies of Vac<sub>Cu</sub> agree well.

## **Electronic** pockets

In Table. I we list the k-points corresponding to the electronic pockets used in Fig. 5 (main paper). These are the k points corresponding to the minima of the corresponding pockets in the dispersion of the lowest conduction band at  $\Delta V = 0$ .

 G. Makov and M. C. Payne, Physical Review B 51, 4014 (1995).



FIG. 6.  $\Delta E_{D(q)}$  versus  $\mu_e - \mu_{VBM}$  graphs for the most stable defects are shown as a function of super-cell sizes for NaSbS<sub>2</sub> (top) and CuSbS<sub>2</sub> (bottom).

- [2] S. Baroni and R. Resta, Physical Review B 33, 7017 (1986).
- [3] C. Persson, Y.-J. Zhao, S. Lany, and A. Zunger, Phys. Rev. B 72, 035211 (2005), URL http://link.aps.org/ doi/10.1103/PhysRevB.72.035211.
- [4] S. Lany and A. Zunger, Phys. Rev. B 78, 235104 (2008), URL http://link.aps.org/doi/10.1103/PhysRevB.78. 235104.
- [5] G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).