

Electronic Supplementary Information - Resonant doping in BiCuSeO thermoelectrics from first principles

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In this work, the density functional theory (DFT) calculations were carried out using the Vienna Ab initio Simulation Package (VASP) within the generalized gradient approximation (GGA)¹ with projector augmented wave (PAW) method²⁻⁴. The DFT + U method was adopted due to the exchange-correlation effects of the strongly localized Cu 3d electrons; the localization of the Cu 3d electrons are usually underestimated within standard DFT⁵. The parameterization by Perdew, Burke and Ernzerhof (PBE) was chosen to calculate the electronic structures of doped BiCuSeO. The effective Coulomb parameter U was set to 4 eV based on the study of Yubo Zhang et al⁶.

The plane wave cutoff energy was set to 500 eV. We employed 9×9×4 k-point meshes generated by the Monkhorst-Pack scheme for numerical integrations over the Brillouin zone of the tetragonal unit cell that contains eight atoms in total. A 3×3×1 supercell containing 72 atoms was constructed with its Brillouin zone sampled with 3×3×4 k-point meshes. One atom in the supercell was substituted, corresponding to a doping concentration of 5.56%. Atomic coordinates were relaxed until the total energy converged to within 10⁻⁵ eV. To perform band unfolding, only the atomic positions in the doping systems were relaxed. Comparing to full relaxations, as can be seen in Fig. s1 and Fig. s2, the two different methods only result in very small differences in both of the formation energies and the DOS. This demonstrates the reliability of the band unfolding technique based on partial relaxation.

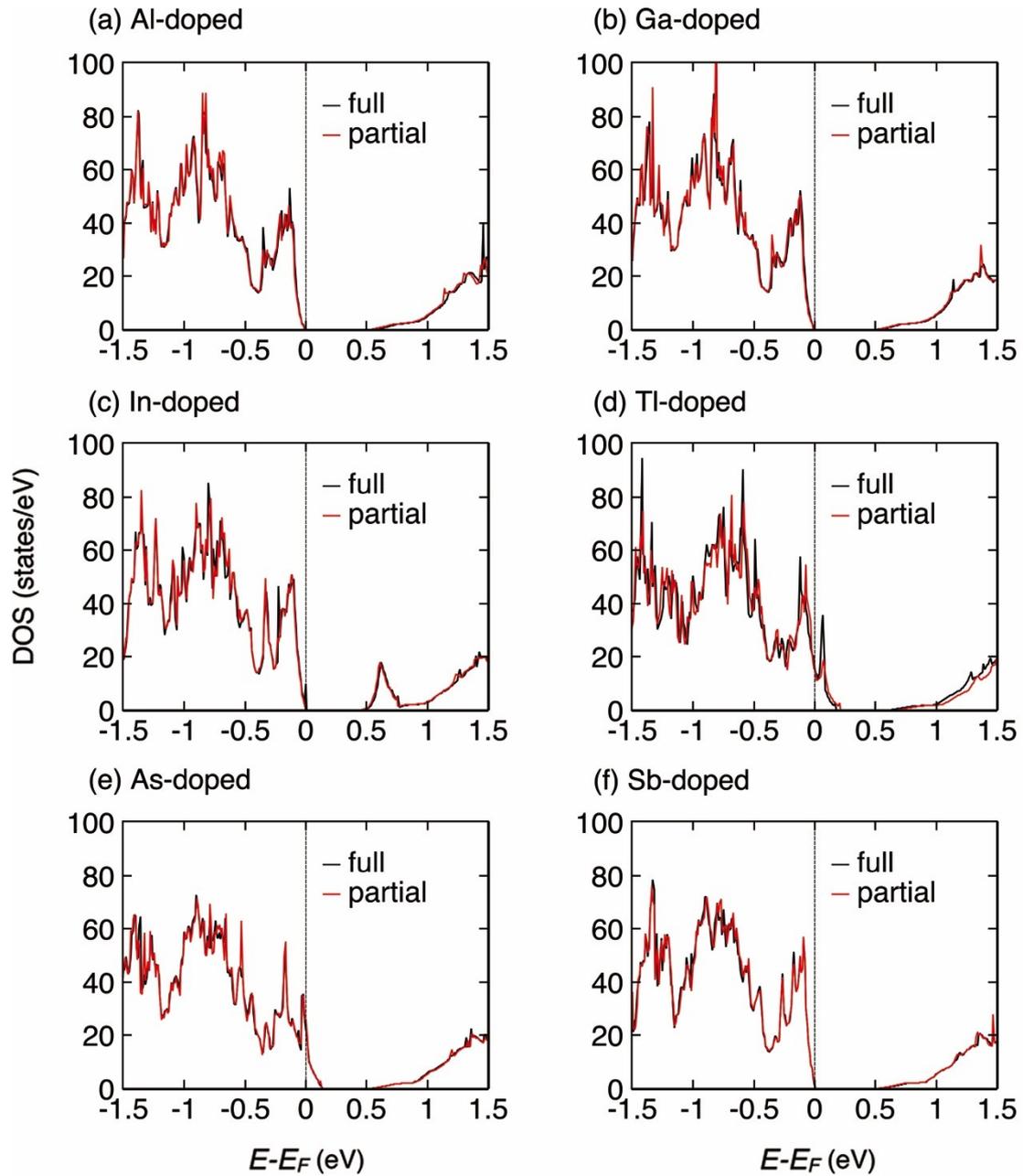


Figure s1 Density of states of (a) Al, (b) Ga, (c) In, (d) Tl, (e) As, and (f) Sb-doped BiCuSeO obtained from full and partial relaxations. Fermi level is located at 0 eV.

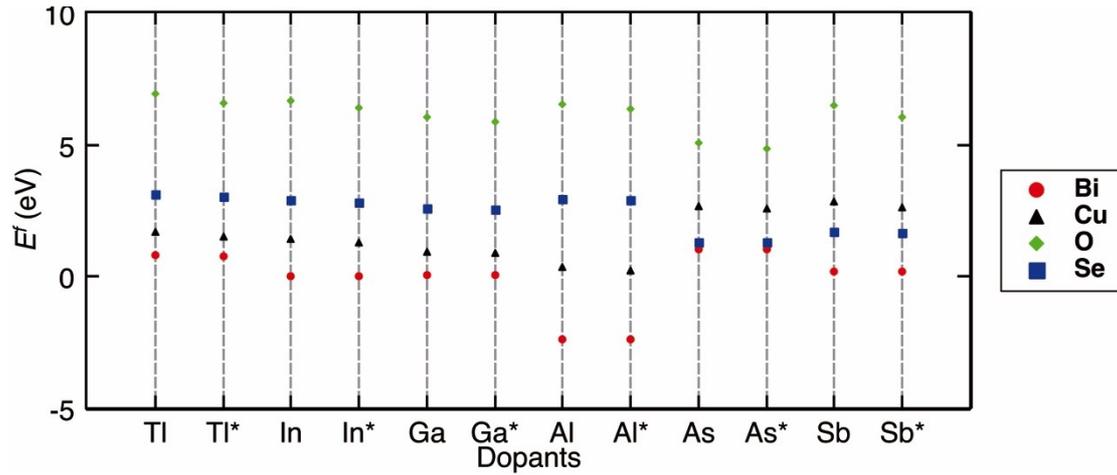


Figure s2 Formation energies of different doped systems calculated from DFT. Elements with and without a star superscript represent full relaxation and partial relaxation, respectively.

The oxidation states of different dopants can be determined based on the lowest formation energies. The valence state of Bi is +3 in BiCuSeO and the common valence states of In are +1 and +3, thus we consider the charge states of 0/-2 when In is doped on the Bi site. The common positive valence states of As and Sb are +3 and +5, thus we consider the charge states of 0/+2 when As or Sb is doped on the Bi site. For the Tl-doped BiCuSeO, Fermi level is fixed because of the resonant states near the valence band maximum; therefore, we have only considered the neutral Tl. On the other hand, as dopants occupy lattice sites other than the Bi site, the systems are no longer intrinsic semiconductors; therefore, only neutral dopants are considered. Based on the above definition, we have calculated the formation energy as a function of Fermi level. It is seen from Fig. s3 that all of the dopants, including In, Sb, and As, tend to take the neutral state when they are doped in BiCuSeO.

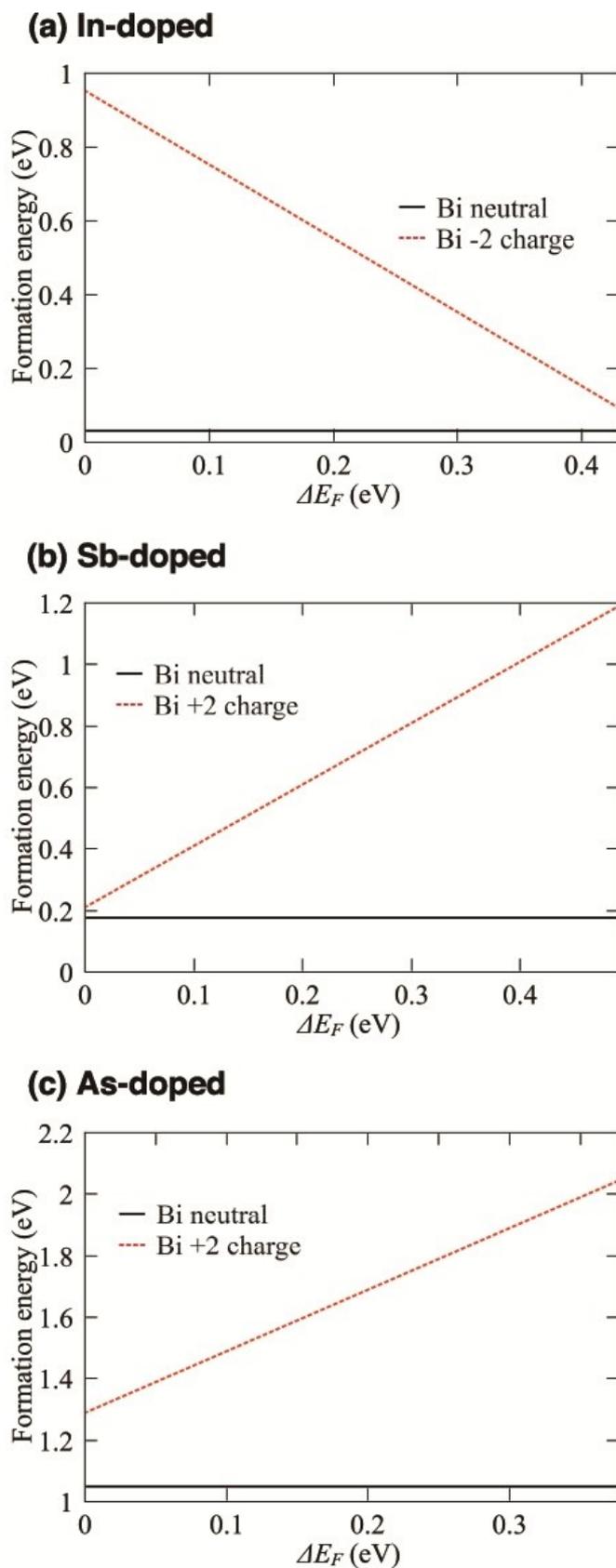


Figure s3 Formation energies of (a) In, (b) Sb, and (c) As-doped BiCuSeO as a function of Fermi level relative to E_V . The maximum values of ΔE_F are taken as the band gaps of the

different doped systems.

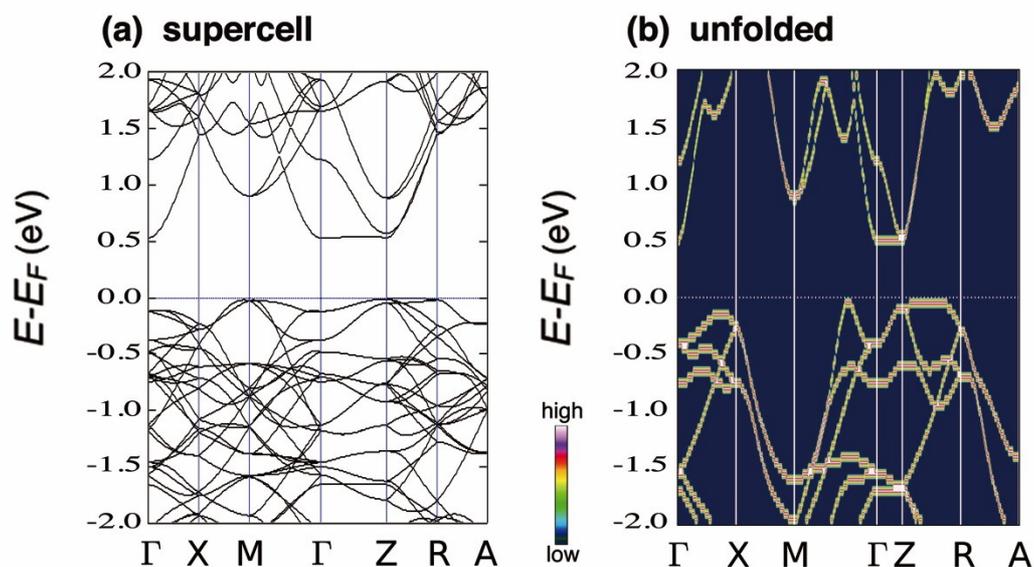


Figure s4 (a) Band structure of BiCuSeO computed from DFT using a $3 \times 3 \times 1$ supercell. (b) Unfolded effective band structure, which can be compared directly to the results of a primitive unit cell. Fermi level is located at 0 eV.

The band structures of large supercells are heavily folded, as can be seen in Fig. s4 (a), making it difficult to analyze. In this work, we applied a recently developed band unfolding technique to recover the primitive cell effective band structure from supercell calculations. As can be seen in Fig. s4 (b), the unfolded effective band structure of pristine BiCuSeO matches exactly with that of the primitive cell. Effective band structure provides a practical way for analyzing complicated band modifications induced by doping.

The unfolded effective band structures of Al, Ga, As and Sb-doped BiCuSeO are shown in Fig. s5, where the doping atoms substitute for their most preferable Bi lattice sites. It is seen that these dopants only induce minor changes on the band structures, in agreement with the DOS results.

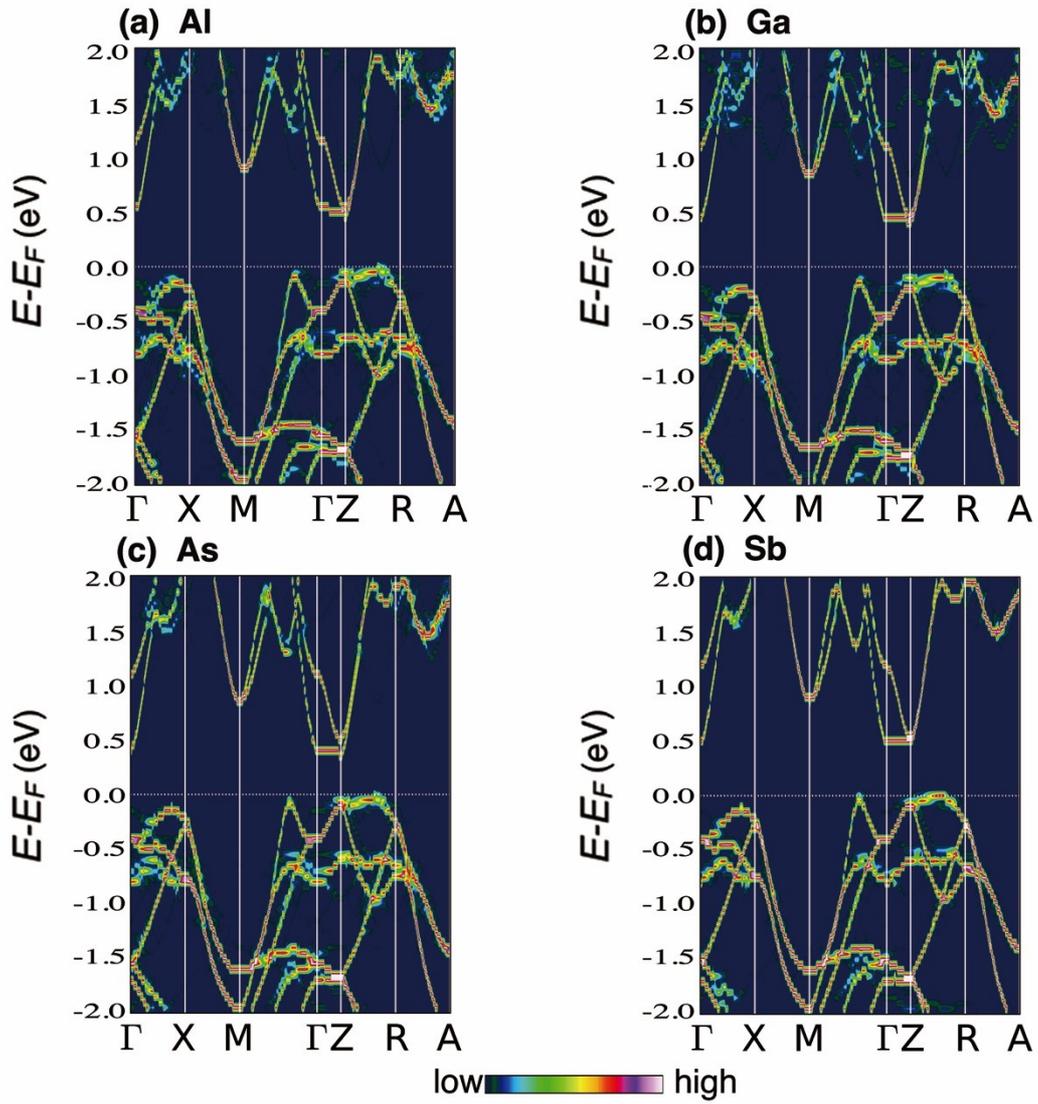


Figure s5 Effective band structures of (a) Al, (b) Ga, (c) As and (d) Sb-doped BiCuSeO, where the doping atoms substitute for their most preferable Bi lattice sites. Fermi level is located at 0 eV.

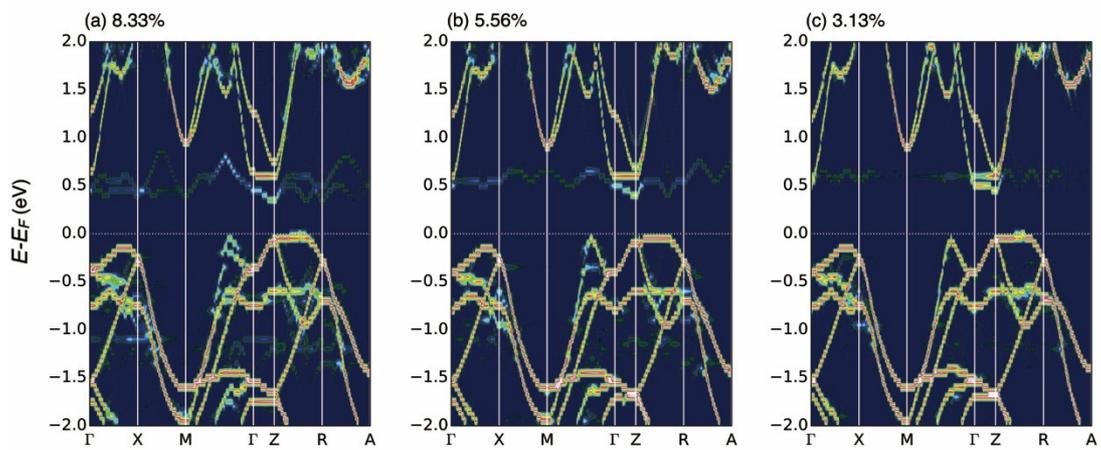


Figure s6 Effective band structures of In-doped BiCuSeO with (a) 8.33%, (b) 5.56%, and (c) 3.13% doping concentrations. Fermi level is located at 0 eV.

The influences of different doping concentrations on resonant states are investigated. The $3 \times 2 \times 1$, $3 \times 3 \times 1$ and $4 \times 4 \times 1$ supercells are constructed to obtain doping concentrations of 8.33%, 5.56% and 3.13%, respectively. As can be seen in Fig. s6, only the weight of the projected resonant states is changed in In-doped BiCuSeO with different doping concentrations. The resonant states still exist even though the doping concentration is low.

References

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