Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supplementary Information for:

Electronic structures and thermoelectric properties of layered oxychalcogenides BiCuO*Ch* (*Ch* = S, Se, and Te): First-principles calculations

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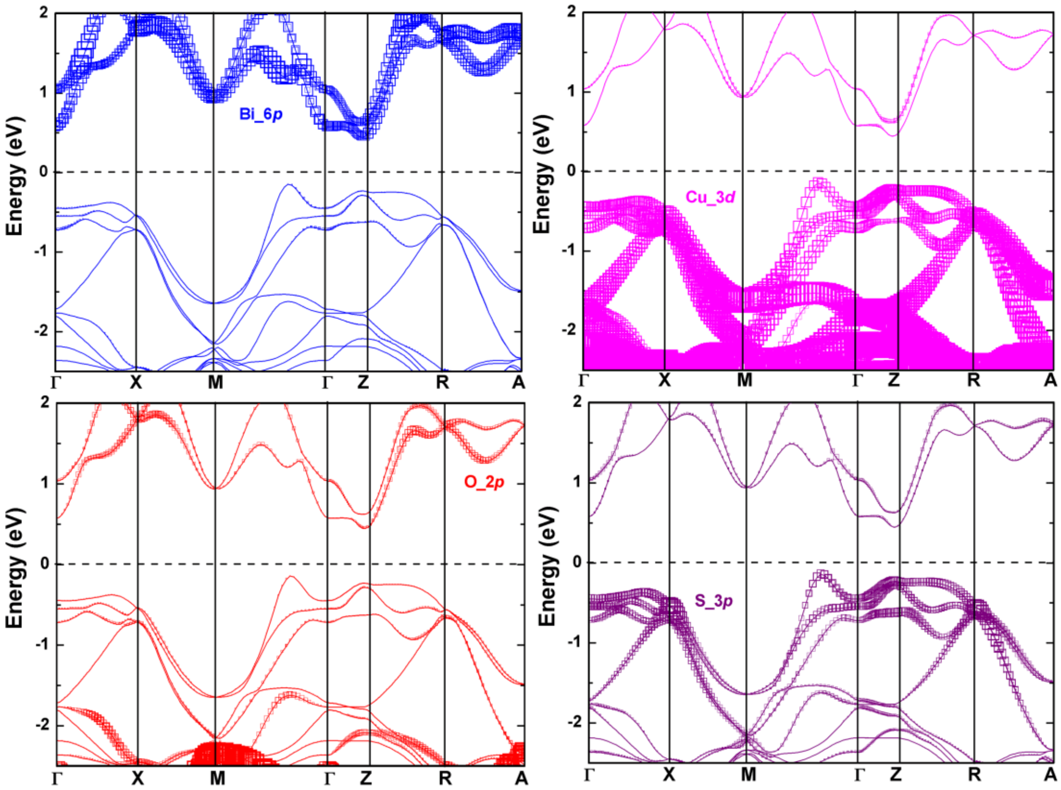
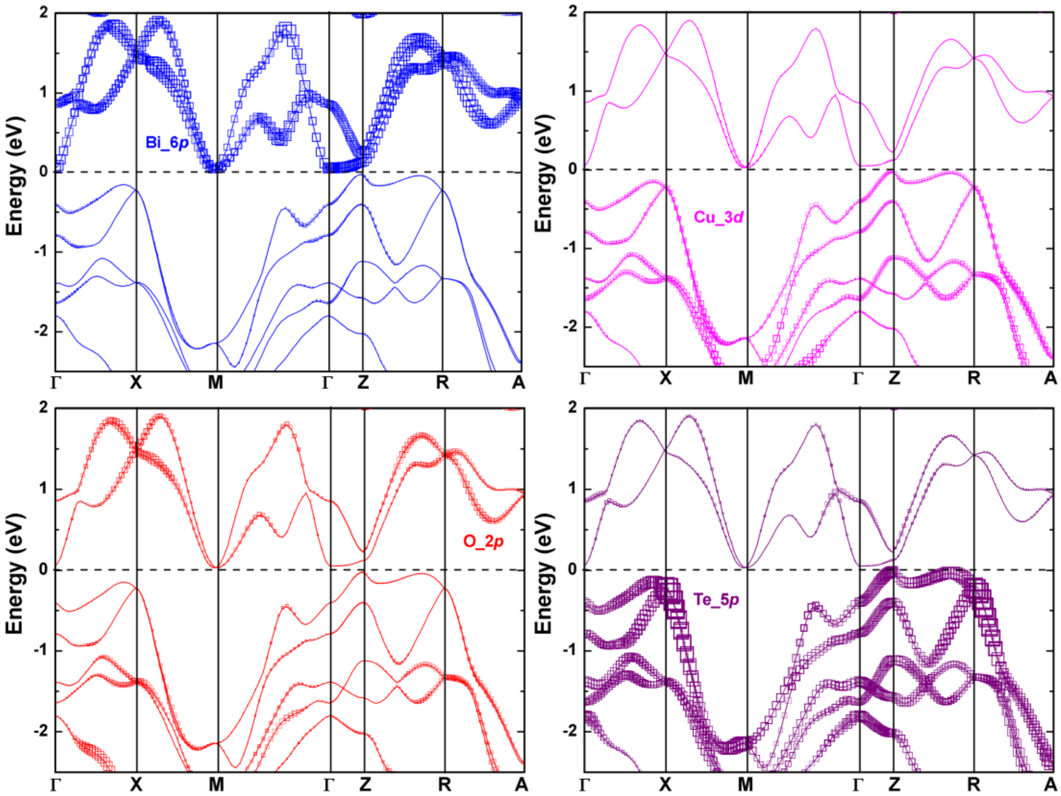


(a) BiCuOS



(b) BiCuOTe

Figure S1 The orbital-decomposed band structures of (a) BiCuOS and (b) BiCuOTe compounds: including the *p*-orbital of Bi (blue), the *d*-orbital of Cu (magenta), the *p*-orbital of O (red) and the *p*-orbitals of S or Te (violet). The Fermi levels are all set to zero.

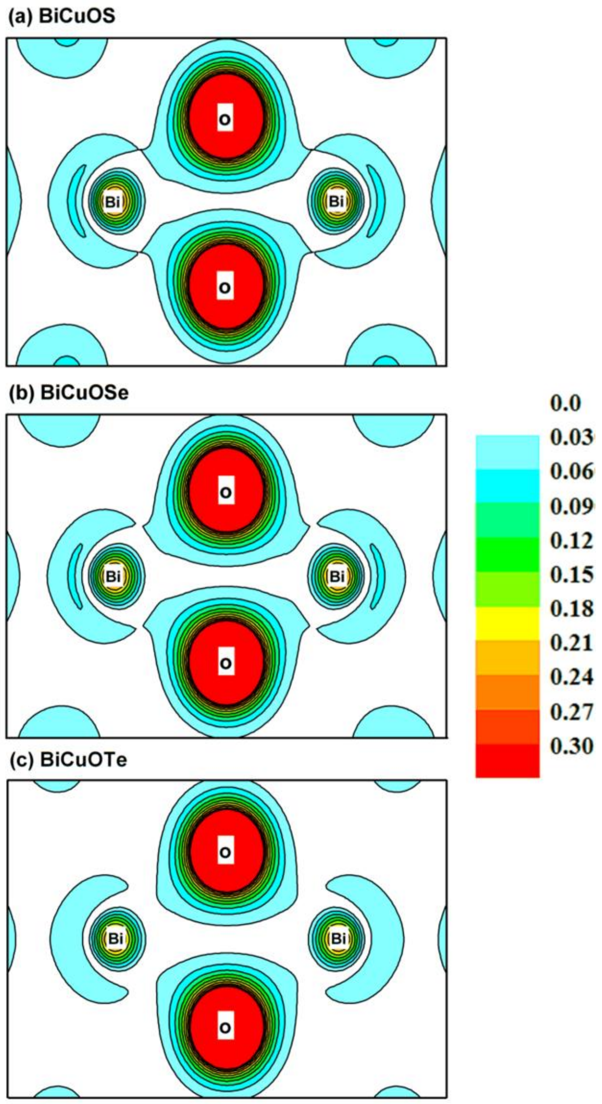


Figure S2. Contour plots of the partial charge density of the valence bands in the energy region of –5 to –2 eV for (a) BiCuOS, (b) BiCuOSe and (c) BiCuOTe on the Bi–O–Bi plane. The Fermi levels are set to zero. The unit of charge density is e/Å^3. The white background means no charge density distributions existing in the area.

As seen in Figure S2, these three compounds have similar partial charge density distributions in the energy region of –5 to –2 eV, and they all show obvious antibonding characteristic between Bi and O states because there is a zero-charge-density gap between them. A lobe-shape charge density on the side of *Ch* atoms points to the $(Cu_2Ch_2)^{2-}$ layer, which can be identified as Bi 6s^2 lone pairs.[1]

[1] R. Seshadri and N. A. Hill, *Chem. Mater.*, 2001, **13**, 2892.