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

Relativistic Electronic Structure and Band Alignment of BiSI and BiSeI: Candidate Photovoltaic Materials

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Supporting Information

Table 1: Calculated lattice parameters of BiSI and BiSeI using the PBE and PBEsol functionals, with and without Grimme's D3 dispersion correction. Percentage difference from experiment in brackets. All cell angles were found to be 90°.

BiSI	a (Å)	b (Å)	c (Å)
PBEsol	8.44 (−0.88 %)	4.13 (−1.00 %)	10.26 (+0.82 %)
PBEsol+D3	8.34 (−2.05 %)	4.14 (−0.73 %)	10.05 (−1.22 %)
PBE	8.81 (+3.46 %)	4.20 (+0.66 %)	10.37 (+10.14 %)
PBE+D3	8.66 (+1.66 %)	4.21 (+1.00 %)	11.21 (+1.94 %)
Experiment	8.52	4.17	10.18
BiSeI	a (Å)	b (Å)	c (Å)
PBEsol	8.63 (−0.83 %)	4.19 (−0.78 %)	10.58 (+0.06 %)
PBEsol+D3	8.53 (−1.90 %)	4.19 (−0.65 %)	10.35 (−2.21 %)
PBE	8.81 (+1.36 %)	4.25 (+0.79 %)	12.03 (+14.35 %)
PBE+D3	8.88 (+2.12 %)	4.28 (+1.34 %)	10.69 (+1.14 %)
Experiment	8.70	4.22	10.57

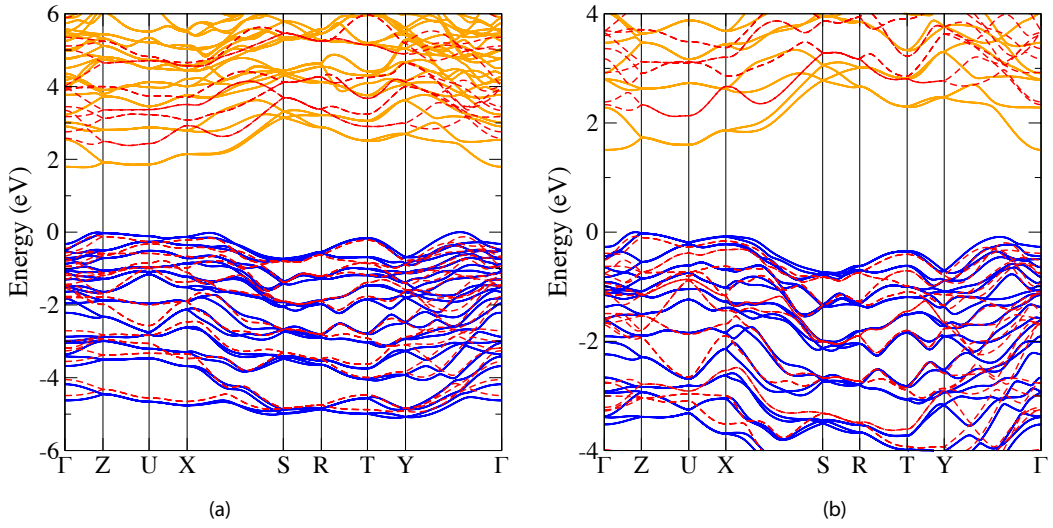

Figure 1: Relativistic renomalisation effect on the band structures of (a) BiSI and (b) BiSeI. The HSE+SOC band structure is shown in blue (valence bands) and orange (conduction bands) with the HSE only band structure shown via dashed red lines.

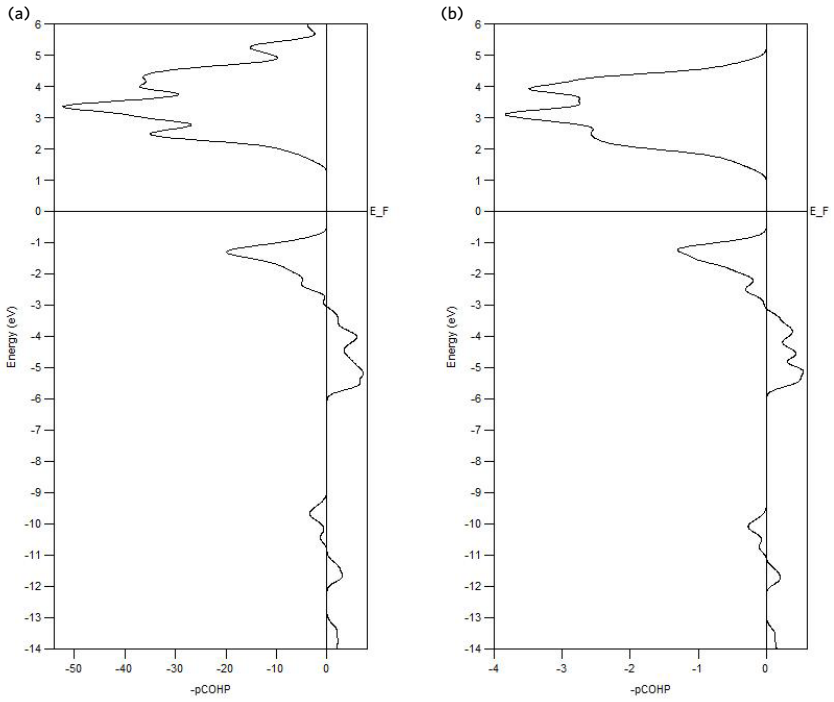

Figure 2: Crystal orbital Hamilton population (COHP) analysis of (a) BiSI and (b) BiSeI, in which the density of states is partitioned, with the sign indicating bonding or antibonding character, and the magnitude related to the strength of the interaction.

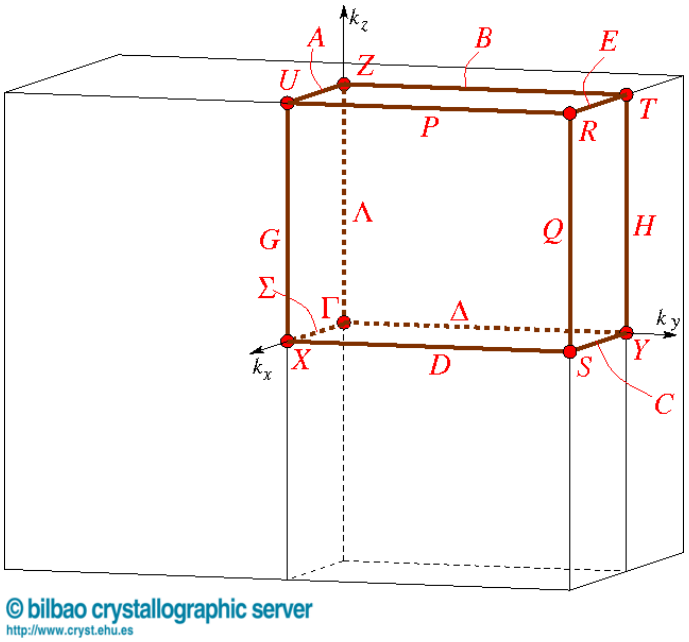

Figure 3: Brillouin zone of the *Pnma* space group. Coordinates of the high symmetry points used for the band structures and effective masses: $\Gamma = (0, 0, 0)$; $\mathrm{Y} = (\frac{1}{2}, 0, 0)$; $\mathrm{X} = (0, \frac{1}{2}, 0)$; $\mathrm{Z} = (0, 0, \frac{1}{2})$; $\mathrm{U} = (0, \frac{1}{2}, \frac{1}{2})$; $\mathrm{T} = (\frac{1}{2}, 0, \frac{1}{2})$; $\mathrm{S} = (\frac{1}{2}, \frac{1}{2}, 0)$; $\mathrm{R} = (0, \frac{1}{2}, \frac{1}{2})$