

Figure 1: High symmetry path in the hexagonal Brillouin zone

ic representations of the crystal structures were generated using the VESTA program [1].

Crystal Structure

$\text{Cs}_3\text{Bi}_2\text{I}_9$ exhibits hexagonal crystal symmetry at room temperature with the space group $P6_3/mmc$ and undergoes a ferroelastic phase transition to a monoclinic structure at 220 K [2]. The hexagonal structure can be considered as a distorted and defect modulated face-sharing perovskite structure in which every third layer of octahedral Bi sites is depleted for charge compensation. Consequently, two neighbouring $[\text{BiI}_6]^{3-}$ octahedrons form a face-sharing $[\text{Bi}_2\text{I}_9]^{3-}$ bi - octahedra which are separated by Cs^+ cations, eventually forming a 0D crystal structure.

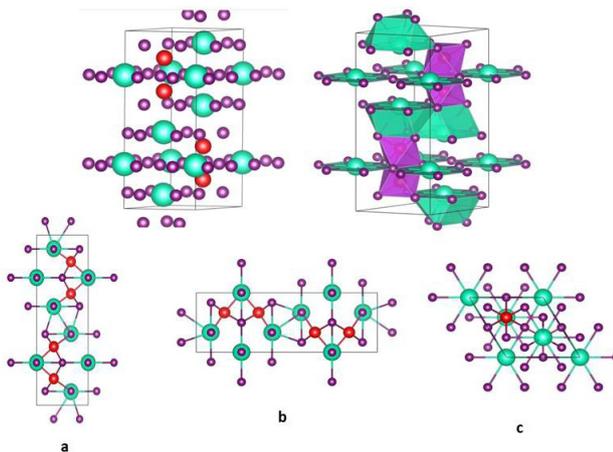


Figure 2: Schematic crystal structure of $\text{Cs}_3\text{Bi}_2\text{I}_9$ (red, green, and violet colours represent Bi, Cs, and I atoms) as seen along (a) a-axis, (b) b-axis, and (c) c-axis

The Density of state and Band Structure of $\text{Cs}_3\text{Bi}_2\text{I}_9$

The VBM is arbitrarily set at 0 eV and is located at the M point. According to our calculations, the electronic bandgap is indirect between Γ and M

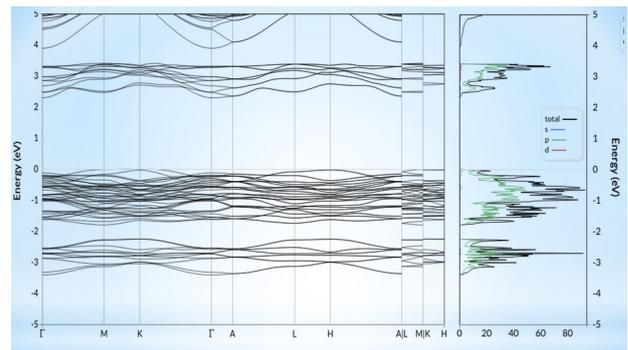


Figure 3: Density of state and band structure of $\text{Cs}_3\text{Bi}_2\text{I}_9$

point. The calculated bandgap value is found to be 2.34 eV.

The orbital contribution of the Cs^+ ion can easily be recognized by the vertical line in the density of state; this indicates that the electronic states of Cs are fully localized in space, without substantial interaction with inorganic biotetrahedra. The valence band of $\text{Cs}_3\text{Bi}_2\text{I}_9$ consists of the predominant contributions from p orbital of I and a little contribution from Bi(s) orbitals. The CBM is composed of nearly equal contributions from I(p) and Bi(p) orbitals. From these results, a paramount feature of this compound emerges: Cs and inorganic $[\text{Bi}_2\text{I}_9]^{3-}$ cages are decoupled from the electronic viewpoint and therefore, Cs do not interfere with the active region of the perovskite. Its only role, regarding the electronic properties, is to donate one electron to the surrounding environment.

References

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