Supplementary Information

Pressure Induced Structural, Electronic and Optical Properties of $CsPbI_3$ Perovskite

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Optical properties calculation:

The optical properties were evaluated from the dielectric function *ε(ω)* given by,

$$\varepsilon(\omega) = \varepsilon_r(\omega) + i\varepsilon_i(\omega)$$

Here $\varepsilon_r(\omega)$ and $\varepsilon_i(\omega)$ denote the real and imaginary part of the dielectric constant. Optical characteristics such as absorption coefficient $\alpha(\omega)$, optical conductivity $\sigma(\omega)$, reflectance $R(\omega)$, energy-loss function $L(\omega)$, extinction coefficient $k(\omega)$ and refractive index $n(\omega)$ can be computed from $\varepsilon_r(\omega)$ and $\varepsilon_i(\omega)$ as follows:

$$\alpha(\omega) = \sqrt{2}\left[\sqrt{\varepsilon_r^2(\omega) + \varepsilon_i^2(\omega)} - \varepsilon_r(\omega)\right]^{1/2}$$

$$\sigma(\omega) = -\frac{i\omega}{4\pi}\varepsilon(\omega)$$

$$R(\omega) = \left|\frac{\sqrt{\varepsilon(\omega)} - 1}{\sqrt{\varepsilon(\omega)} + 1}\right|^2$$

$$L(\omega) = \frac{\varepsilon_i(\omega)}{\varepsilon_r^2(\omega) + \varepsilon_i^2(\omega)}$$

$$K(\omega) = \frac{\left[\sqrt{\varepsilon_r^2(\omega) + \varepsilon_i^2(\omega)} - \varepsilon_r(\omega)\right]^{1/2}}{2}$$

$$n(\omega) = \frac{\left[\sqrt{\varepsilon_r^2(\omega) + \varepsilon_i^2(\omega)} + \varepsilon_r(\omega)\right]^{1/2}}{2}$$

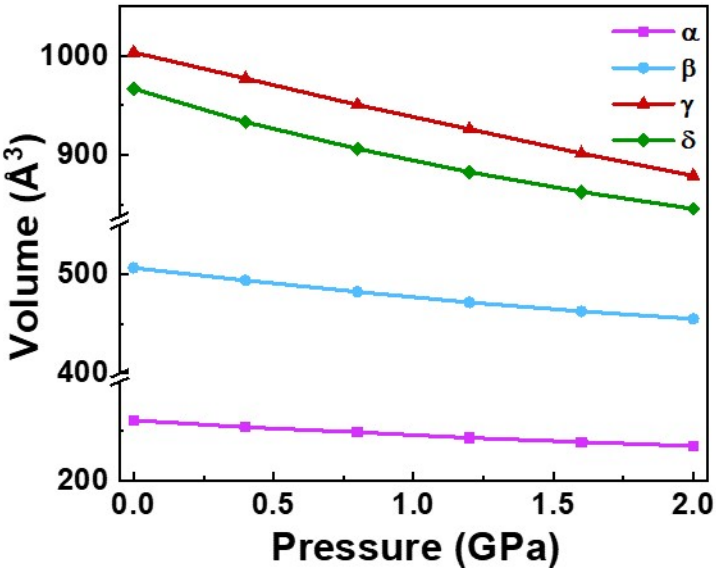

Figure S1. Variation of unit cell volume of α-, β-, γ- and δ-$CsPbI_3$ perovskite with applied pressure.

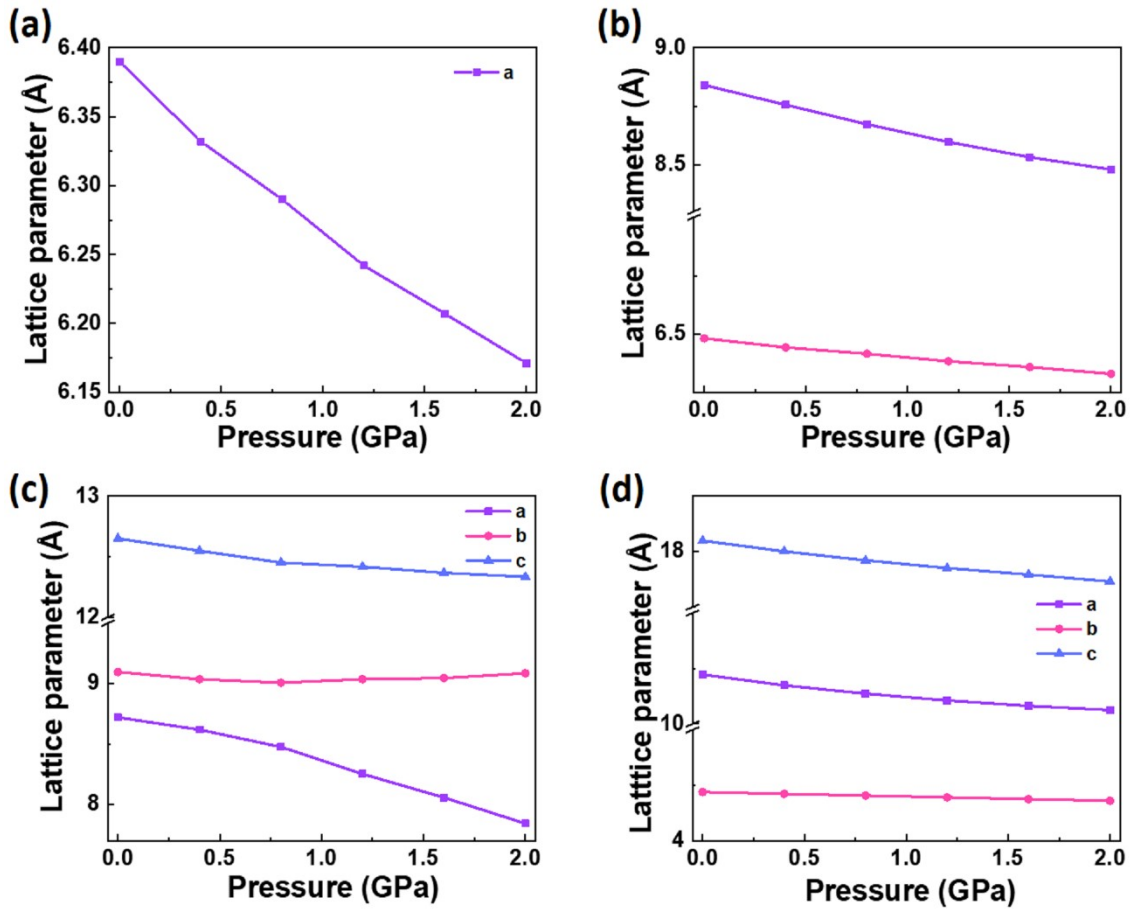

Figure S2. Lattice parameter evolution as a function of applied pressure: (**a**) α-, (**b**) β- (**c**) γ- and (**d**) δ-phases of $CsPbI_3$.

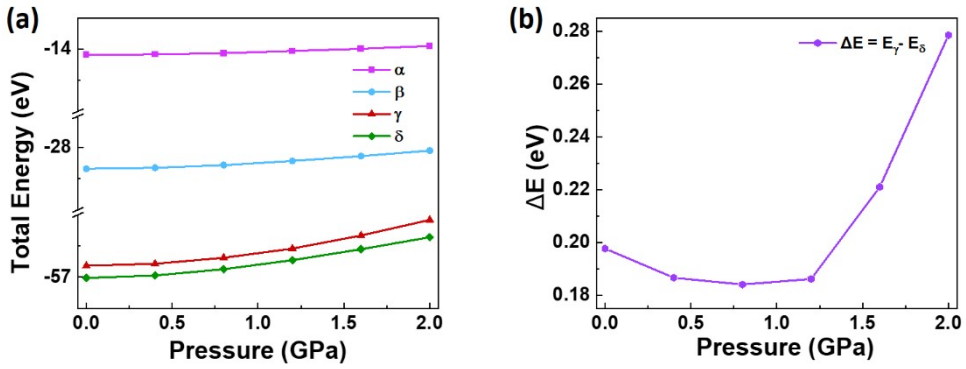

Figure S3. (a) Computed total energy of unit cells for α-, β-, γ-, and δ-phases of $CsPbI_3$ and (**b**) Total energy difference between the unit cells of γ- and δ-$CsPbI_3$ ($\Delta E = E_\gamma - E_\delta$) as a function of applied pressure.

Table S1. Calculated lattice parameters of $CsPbI_3$ polymorphs with pressure using PBE functional.

Pressure	α	β		γ			δ		
(GPa)	a	a	c	a	b	c	a	b	c
0	6.39	8.841	6.481	8.72	9.096	12.651	10.891	4.877	18.20
0.4	6.332	8.756	6.442	8.618	9.036	12.549	10.696	4.845	18.006
0.8	6.29	8.673	6.415	8.475	9.007	12.452	10.547	4.815	17.845
1.2	6.242	8.597	6.383	8.252	9.036	12.417	10.424	4.782	17.706
1.6	6.207	8.532	6.358	8.057	9.046	12.367	10.324	4.75	17.588
2	6.171	8.479	6.329	7.842	9.085	12.334	10.251	4.722	17.463

Table S2. Calculated band gaps of α-, β-, and γ-phases of $CsPbI_3$ as a function of pressure using PBE functional with and without SOC consideration.

Pressure	α		β		γ	
(GPa)	**PBE**	**PBE+SOC**	**PBE**	**PBE+SOC**	**PBE**	**PBE+SOC**
0	1.4782	0.3688	1.5808	0.6675	1.8070	0.8379
0.4	1.3982	0.2980	1.5196	0.6389	1.7791	0.8492
0.8	1.3361	0.2410	1.4715	0.6336	1.7666	0.8492
1.2	1.2572	0.1698	1.4131	0.6084	1.7663	0.8794
1.6	1.1971	0.1139	1.3592	0.5841	1.7766	0.9160
2	1.1329	0.0541	1.3043	0.5479	1.7977	0.9632

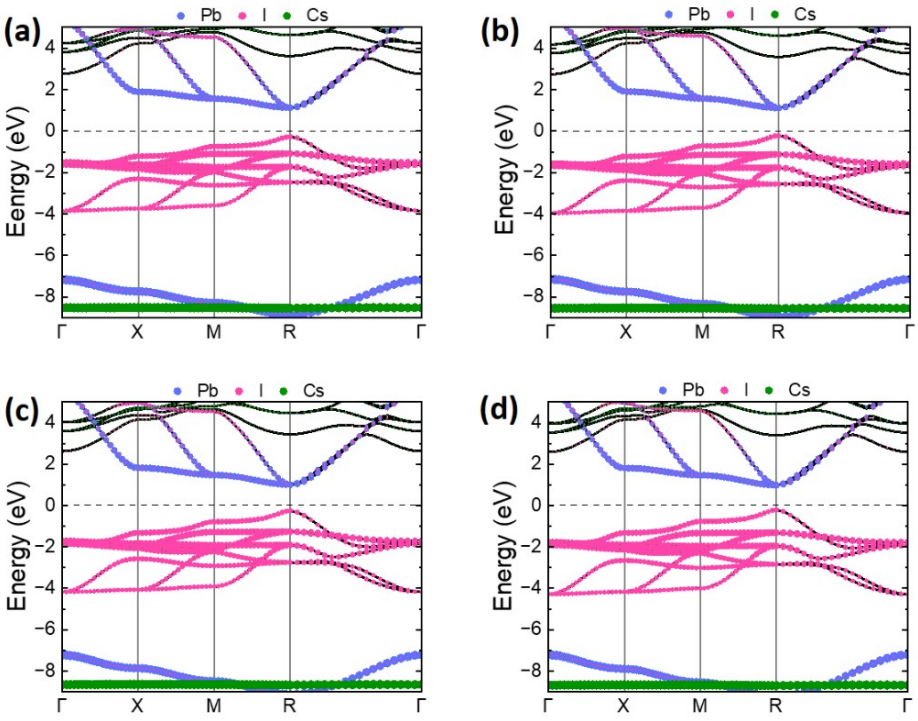

Figure S4. Calculated projected band structures of α-$CsPbI_3$ with applied pressure: (**a**) 0.4 GPa, (**b**) 0.8 GPa, (**c**) 1.2 GPa and (**d**) 1.6 GPa.

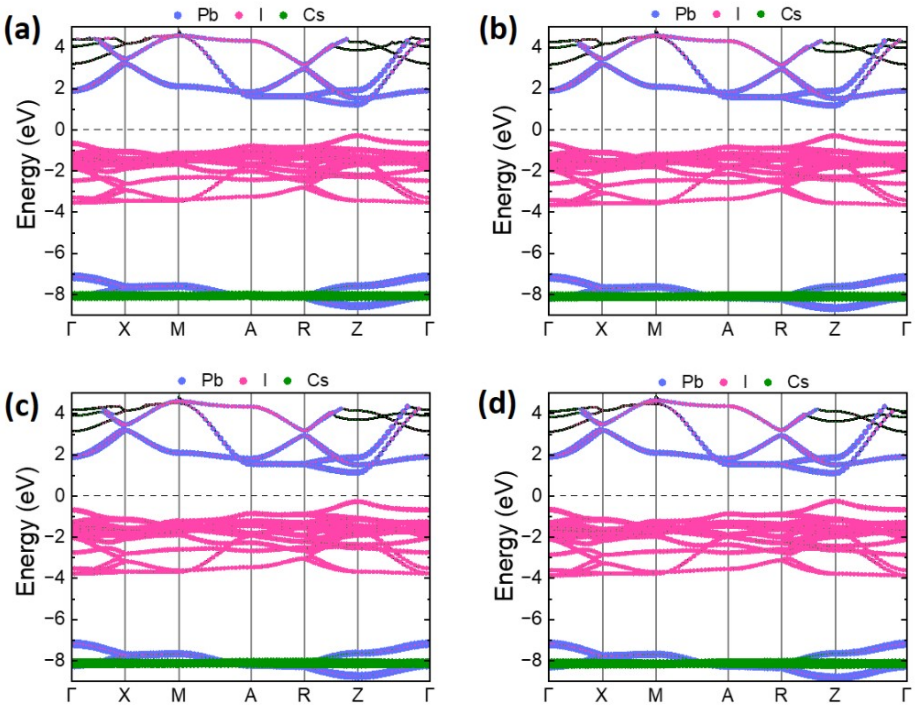

Figure S5. Calculated projected band structures of β-$CsPbI_3$ with applied pressure: (**a**) 0.4 GPa, (**b**) 0.8 GPa, (**c**) 1.2 GPa and (**d**) 1.6 GPa.

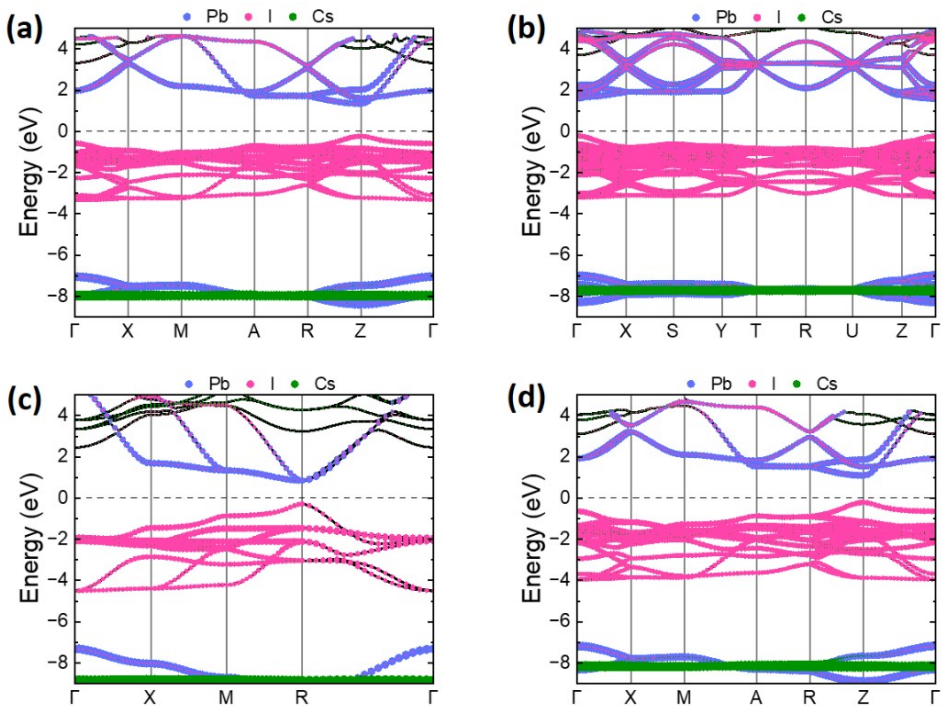

Figure S6. Calculated projected band structures of γ-$CsPbI_3$ with applied pressure: (**a**) 0.4 GPa, (**b**) 0.8 GPa, (**c**) 1.2 GPa and (**d**) 1.6 GPa.

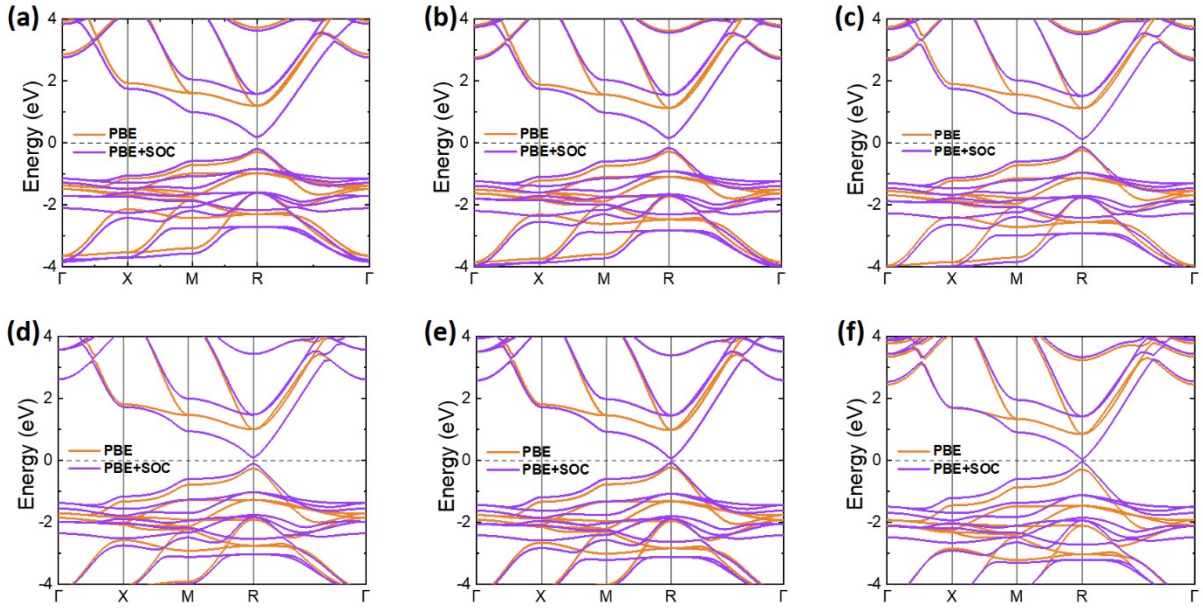

Figure S7. Computed band structures of α-$CsPbI_3$ with and without SOC effect at various applied pressures: (**a**) 0 GPa, (**b**) 0.4 GPa, (**c**) 0.8 GPa, (**d**) 1.2 GPa, (**e**) 1.6 GPa and (**f**) 2 GPa

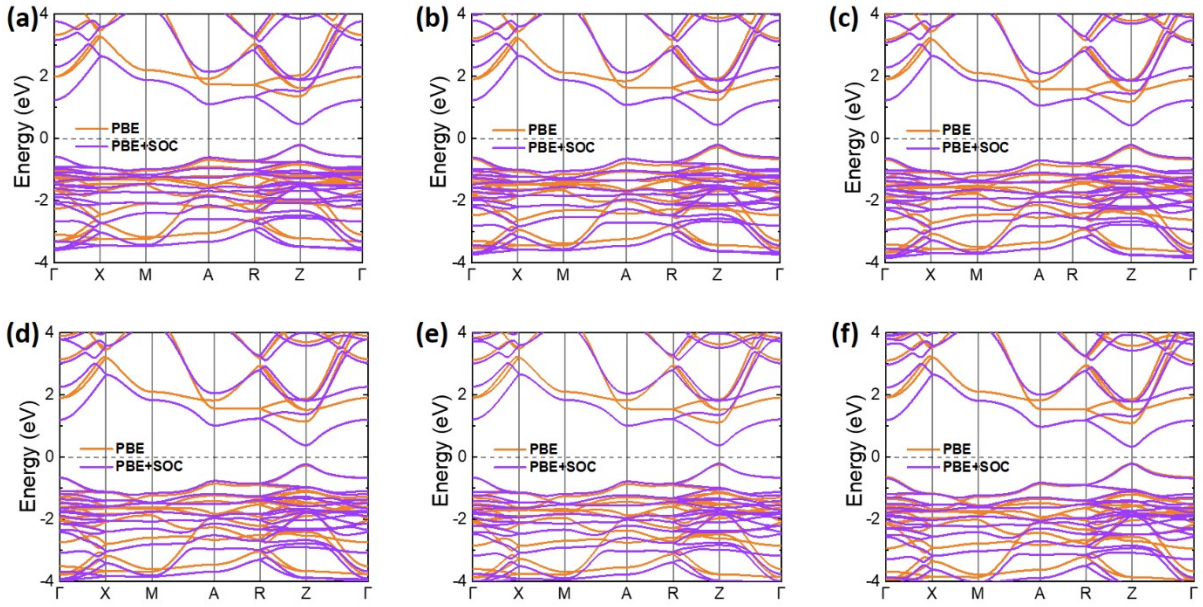

Figure S8. Computed band structures of β-$CsPbI_3$ with and without SOC effect at various applied pressures: (**a**) 0 GPa, (**b**) 0.4 GPa, (**c**) 0.8 GPa, (**d**) 1.2 GPa, (**e**) 1.6 GPa and (**f**) 2 GPa

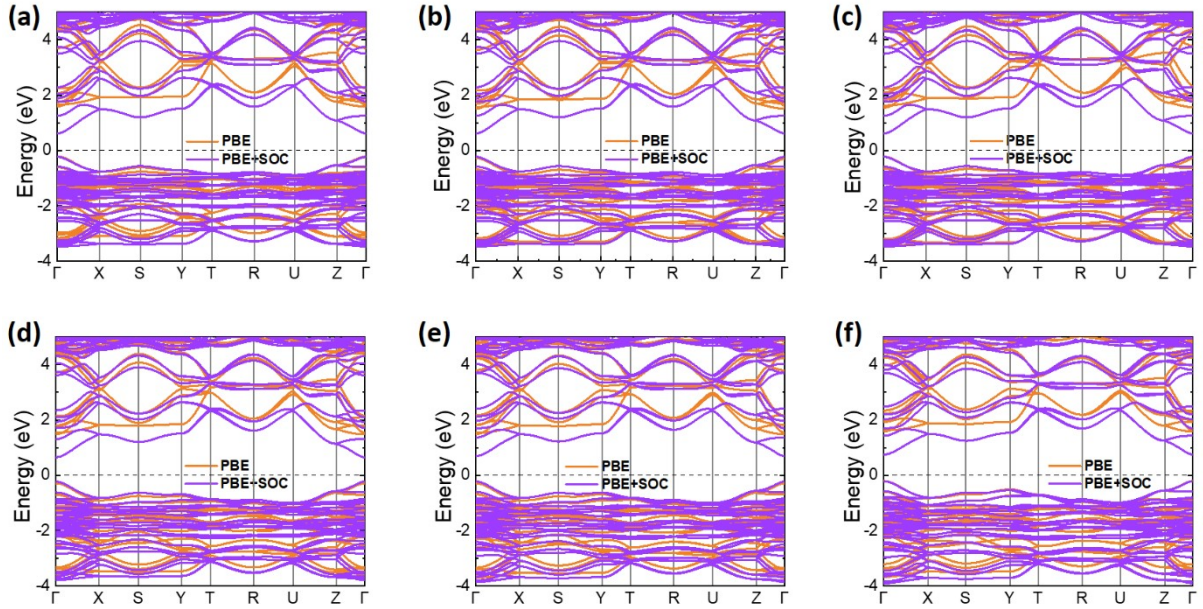

Figure S9. Computed band structures of γ-$CsPbI_3$ with and without SOC effect at various applied pressures: (**a**) 0 GPa, (**b**) 0.4 GPa, (**c**) 0.8 GPa, (**d**) 1.2 GPa, (**e**) 1.6 GPa and (**f**) 2 GPa

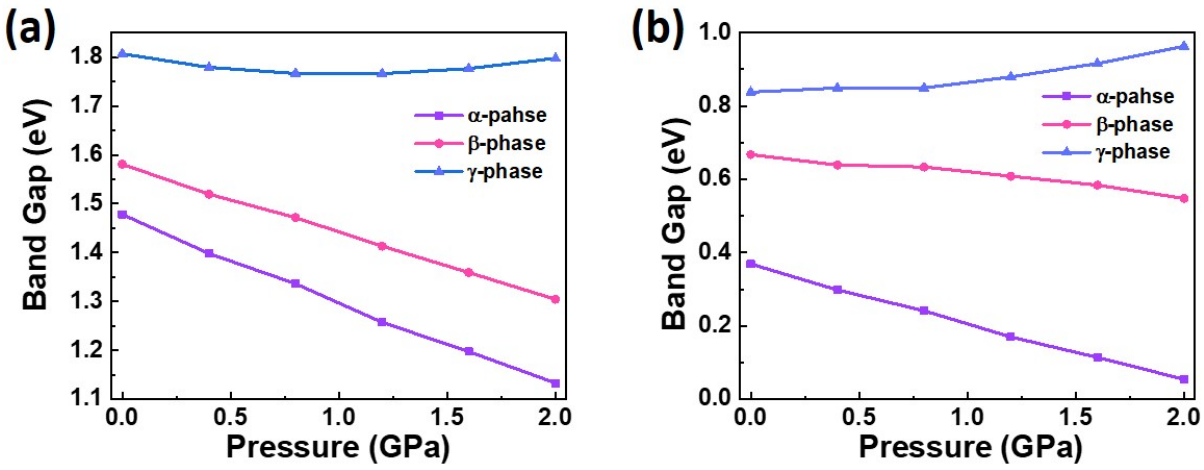

Figure S10. Variation of band gap (**a**) without and (**b**) with SOC effect as a function of applied pressure

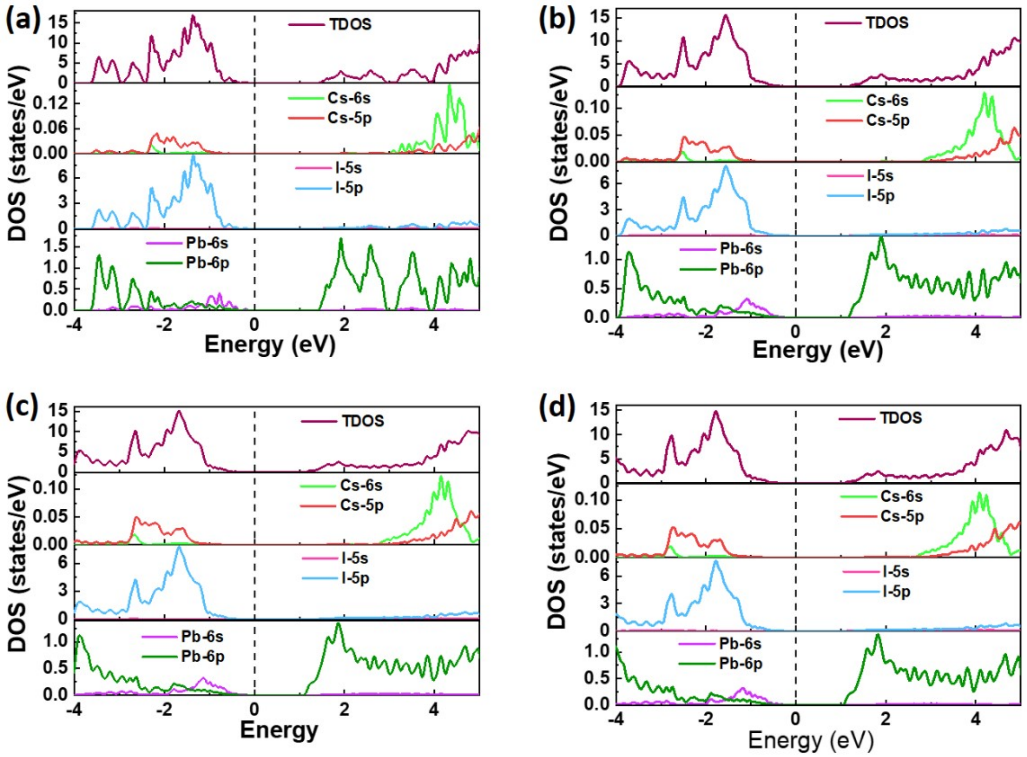

Figure S11. Computed PDOS of α-$CsPbI_3$ with applied pressure: (**a**) 0.4 GPa, (**b**) 0.8 GPa, (**c**) 1.2 GPa and (**d**) 1.6 GPa.

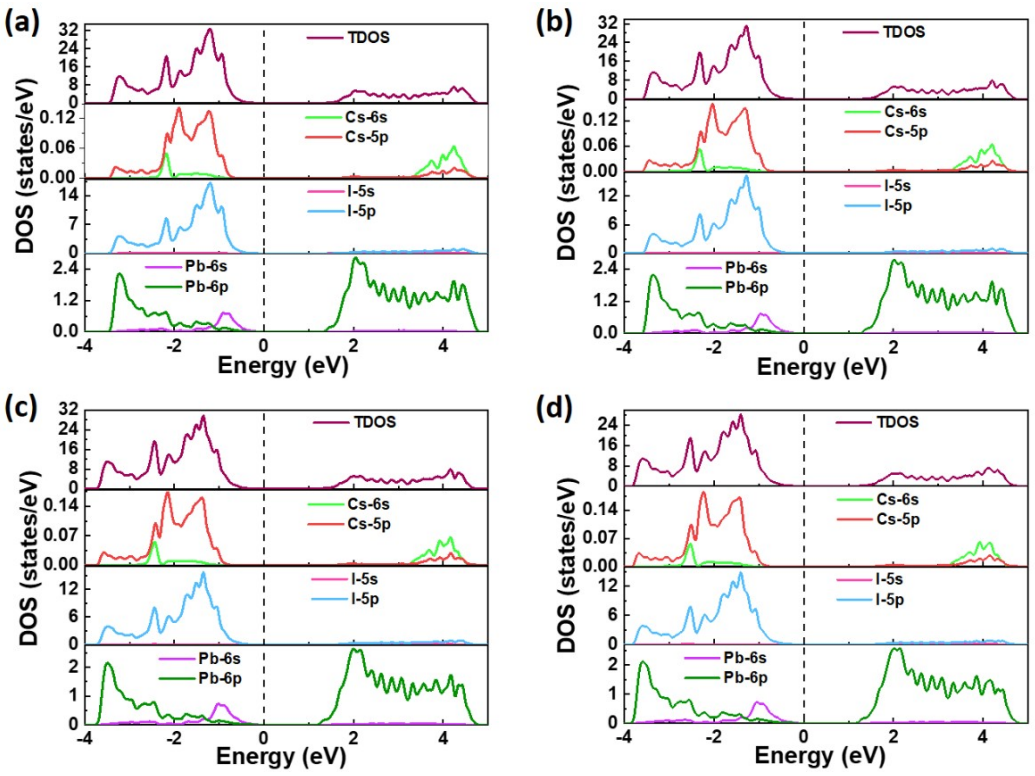

Figure S12. Computed PDOS of β-$CsPbI_3$ with applied pressure: (**a**) 0.4 GPa, (**b**) 0.8 GPa, (**c**) 1.2 GPa and (**d**) 1.6 GPa.

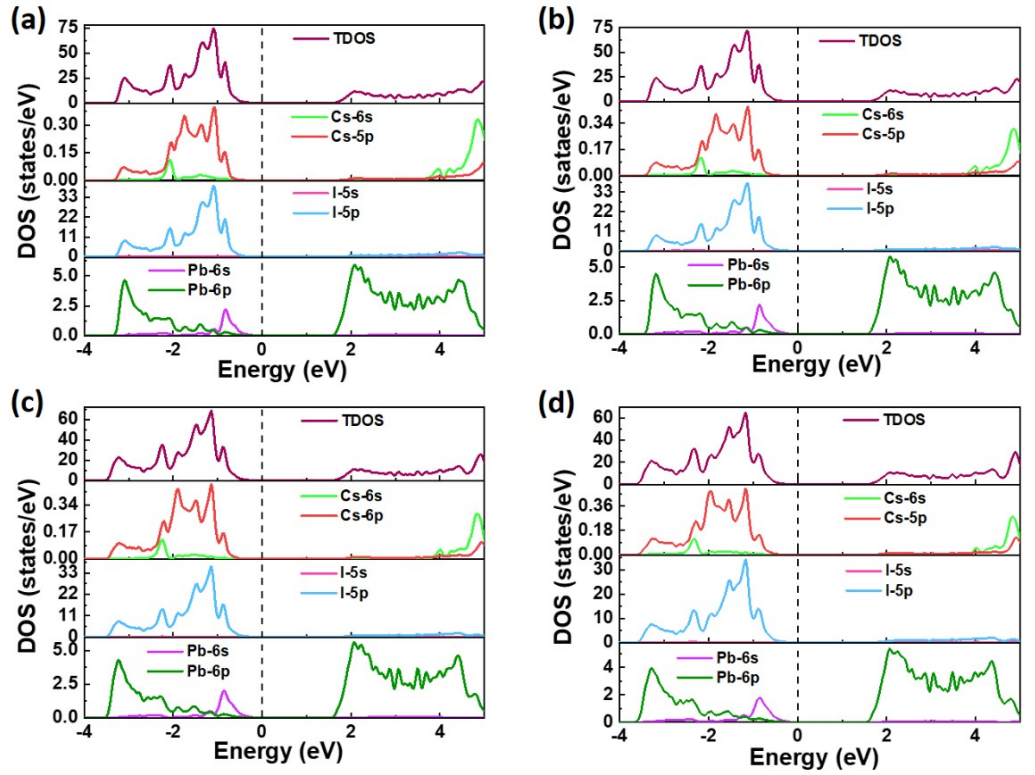

Figure S13. Computed PDOS of γ-$CsPbI_3$ with applied pressure: (**a**) 0.4 GPa, (**b**) 0.8 GPa, (**c**) 1.2 GPa and (**d**) 1.6 GPa.

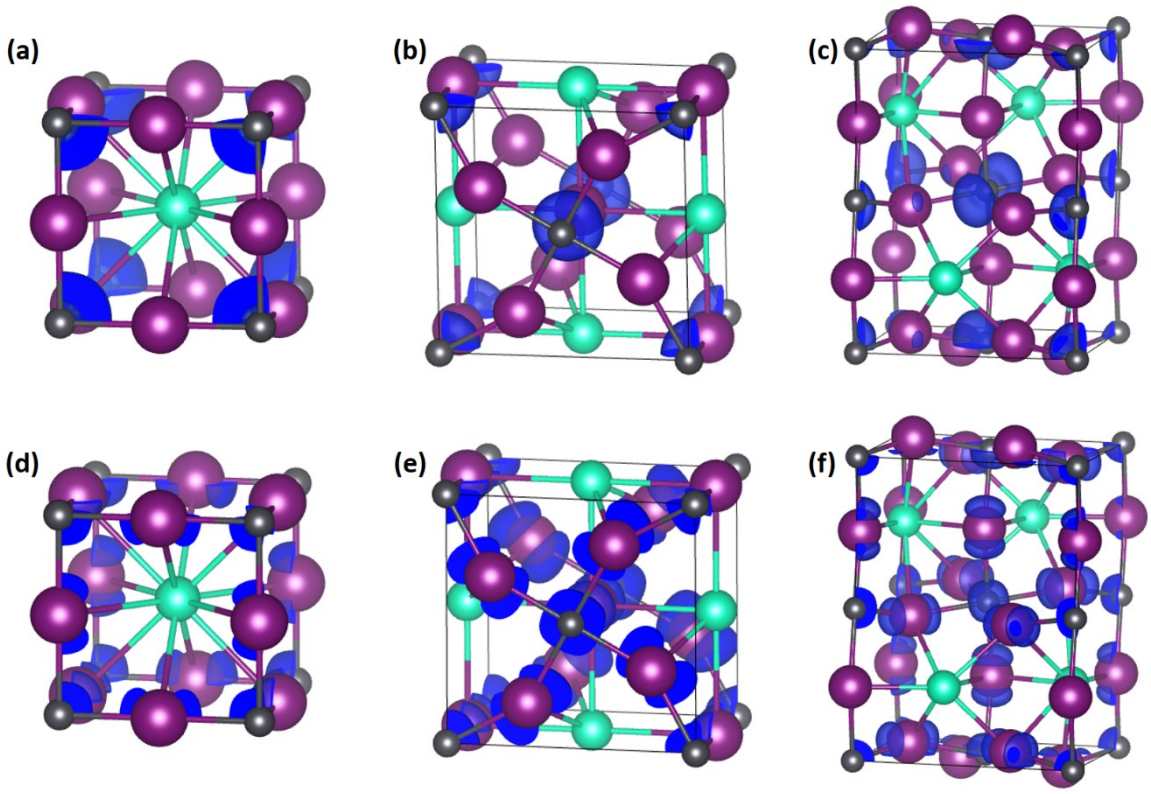

Figure S14. Computed charge densities at CBM (upper row) and VBM (bottom row) for α-(**a**, **d**), β-(**b**, **e**), and γ-(**c**, **f**) phases of $CsPbI_3$ at 0 GPa.