Supplementary Information

Impact of biaxial strain on structural, electronic and optical properties of photocatalytic bulk bismuth oxyhalides

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Section S1

The bulk crystal structure of BiOX belongs to the tetragonal space group $P4/nmm$ (No. 129), known as the matlockite crystal structure. The first-principles calculations on bulk crystal structures were done using density functional theory (DFT), including spin-orbit coupling (SO) and dispersion energy corrections arising from the van der Waals (vdW) interactions solved within DFT-D3 formulations,[3] as implemented in plane-wave basis Vienna Ab-initio Simulation package (VASP).[4–6] We have used Perdew-Burke-Ernzerhof (PBE) formulation of the exchange-correlation within generalized gradient approximation (GGA). In order to discuss the details of their bulk structural geometry compared to respective the ex-

perimental data, we have tabulated their crystal structural details in the Table 1. We have analyzed few important parameters, namely d_s: the inter-planer separation of X-Bi-Bi-O-X laminar; d_X: the width of the laminar sandwiched between two halide X atomic layers, d_{Bi}: the separation of Bi-Bi atomic layers, and in-plane angle <Bi-O-Bi within the laminar.

Table 1: The optimized bulk crystal structures of BiOX (X; F, Cl, Br, I) using PBE-GGA+vdW+SO formalism, compared with experimental data. Experimental data is taken from References [1,2]

System	Structural Parameters	Experimental	PAW PBE-GGA+vdw-D3 Optimization
BiOF	d_s(Å)	1.90	1.80
	d_X(Å)	4.33	4.39
	d_{Bi}(Å)	2.59	2.61
	Bi-X (Å)	2.80	2.81
	Bi-O (Å)	2.28	2.29
	<Bi-O-Bi	110.8°	110.5°
BiOCl	d_s(Å)	2.16	2.15
	d_X(Å)	5.19	5.20
	d_{Bi}(Å)	2.51	2.55
	Bi-X (Å)	3.01	3.07
	Bi-O (Å)	2.31	2.34
	<Bi-O-Bi	114.2°	113.5°

System	Structural Parameters	Experimental	PAW PBE-GGA+vdw-D3 Optimization
BiOBr	d_s(Å)	2.43	2.48
	d_X(Å)	5.68	5.61
	d_{Bi}(Å)	2.48	2.53
	Bi-X (Å)	3.20	3.19
	Bi-O (Å)	2.32	2.34
	<Bi-O-Bi	115.3°	114.4°
BiOI	d_s(Å)	3.05	2.95
	d_X(Å)	6.09	6.13
	d_{Bi}(Å)	2.41	2.48
	Bi-X (Å)	3.38	3.38
	Bi-O (Å)	2.34	2.36
	<Bi-O-Bi	117.9°	116.6°

Section S2

The biaxial strain was applied to the in-plane lattice parameters of the bulk BiOX structures, in order to create the uni-axial pressure on the lattice. Both compressive and tensile strains were applied to these PBE-GGA+vdW+SO optimization of the known experimental *ab*-lattice parameters. Details of the lattice parameters are tabulated in Table 2. In case of the tensile strain, the *ab*-lattice parameters were equally stretched and for compressive strain they were equally compressed. The strained structures were relaxed without changing the cell volume.

Table 2: The details of compressive and tensile strained lattice parameters used for the calculations.

Bulk Structures	Out-of-plane lattice parameter *c* in Å	In-plane lattice parameters *a=b* in Å	2% Tensile strain *a=b* in Å	2% Compressive strain *a=b* in Å
BiOF	6.188	3.767	3.843	3.692
BiOCl	7.359	3.910	3.988	3.832
BiOBr	8.102	3.944	4.022	3.865
BiOI	9.100	4.019	4.099	3.939

Section S3

The dynamical stability of these BiOX systems with and without the applied in-plane strain are verified through the study of their phonon total DOS and bands dispersion. Using density functional perturbation theory (DFPT) as in the VASP code, the dynamical matrices for a given displacement 0.01Å on the lattices were calculated by the PBE-GGA+vdW+SO formalism over the supercell of size $4 \times 4 \times 3$ of the bulk BiOX structures. The phonon DOS and bands dispersion plots are done using the PHONOPY interface. During the phonon DOS and bands dispersion calculations, we have used 109800 irreducible q-points on sampling mesh. In Figure 1, the calculated phonon total DOS of 2% compressive strained bulk systems BiOF (top left), BiOCl (top right), BiOBr(bottom left) and BiOI(bottom right) over their PBE-GGA+vdW+SO optimized crystal structures are shown.

From these DOS plots, it is quite obvious that the compressive strain helps BiOF to be more stable dynamically by removing the negative modes from the below zero frequency range compared to the unstrained counter part, whereas the other BiOX bulk systems almost retain their lattice stability within this applied compressive strain limit, having no negative modes.

In a similar scenario, we have also applied the 2% tensile strain on the in-plane lattice of each BiOX system and analyzed their phonon DOS as shown in Figure 2. It is very much sure that all of these bulk phases do not allow same amount (2%) of tensile strain over

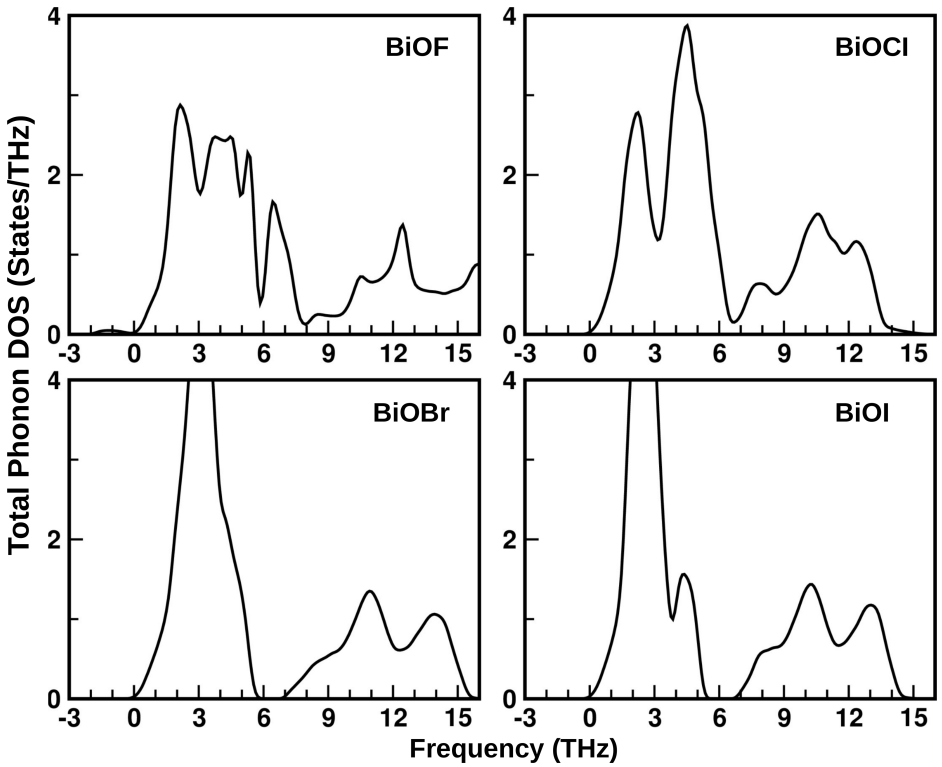

Figure 1: The calculated total phonon DOS plots for 2% compressive strained BiOX bulk systems using PBE-GGA+vdW+SO formalism.

their experimental or PBE-GGA-vdW+SO optimized structures, as we see negative phonon modes below zero for all cases. Specially, as it is visible that the negative modes become more prominent in case of BiOF upon tensile strain application and also, it is reasonably visible for other systems below the zero frequency regime. So, we have ruled out the investigation of tensile strained structures, from current scenario.

Section S4

The effective mass (m^*) of photoexcited charge carriers of all the BiOX bulk phases are estimated for their unstrained and compressive strained structures. The second derivatives at each energy of the two bands corresponding to the HOMO and LUMO have been calculated using the central difference method of numerical differentiation. Figure 3 shows the plot of second derivatives (SD) at all energies for the two bands. The values of SD at HOMO and

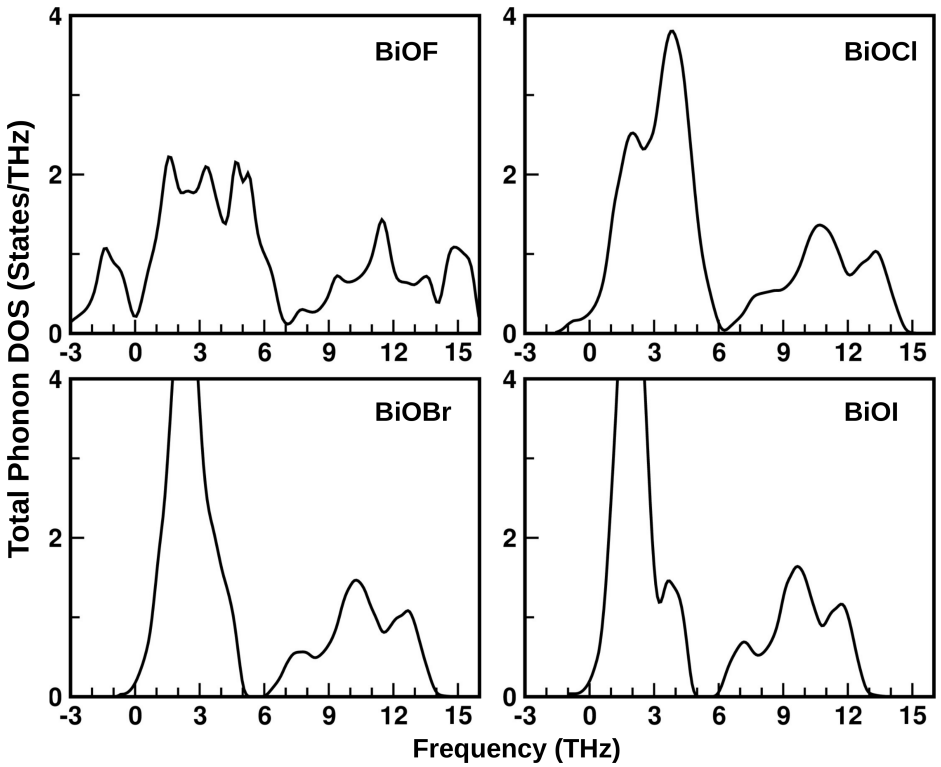

Figure 2: The calculated total phonon DOS plots for 2% tensile strained BiOX bulk systems using PBE-GGA+vdW+SO formalism.

LUMO extrema are marked with cross sign on the plots. The accuracy and the validity of the approach have been discussed else where.[8,9] We have used the electronic band structures of these systems calculated through the PBE-GGA+vdW+SO formalism in DFT.

Section S5

The calculated dielectric function of unstrained and compressive strained bulk crystal structures of BiOX (X: F, Cl, Br, I) are shown in Figure 4. All calculations of optical properties are done using WIEN2K code,[10] over their PBE-GGA+vdW+SO optimized bulk structures within the linear optical limit and without consideration of electron-hole interactions. The optical band-gaps were estimated by taking a tangent at the most linear region using similar way like Tauc plot of absorption spectra in the experimental context.

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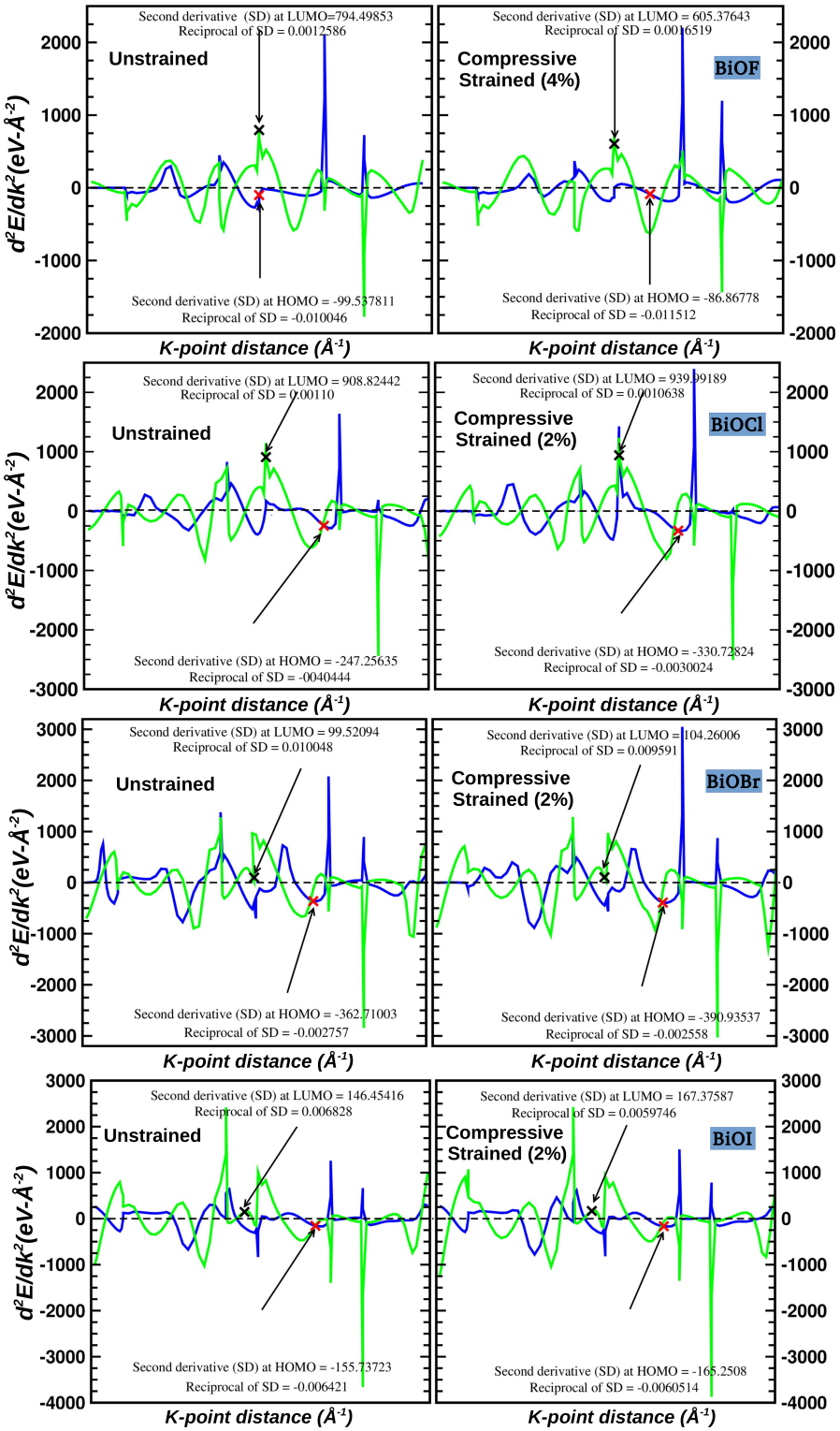

Figure 3: The calculated second derivative (SD) at the band-edges extrema of HOMO and LUMO for BiOF, BiOCl, BiOBr, BiOI respectively from top to bottom.

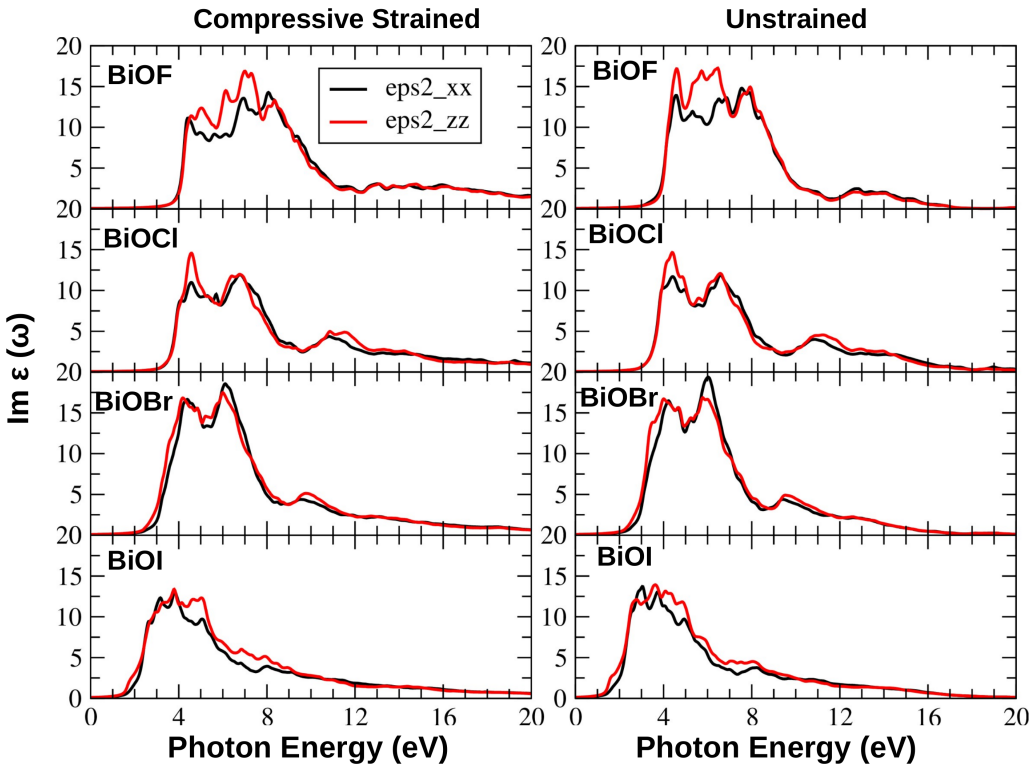

Figure 4: The calculated imaginary part of dielectric function, Im (ω) for 2% compressive strained BiOX bulk systems (4% for BiOF) using PBE-GGA+vdW+SO formalism optimized bulk crystal structures are shown. With black solid line light polarization parallel to the in-plane and red solid lines light polarization perpendicular to the in-plane contribution of dielectric function.