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Electronic Supplementary Information for

Temperature-dependence of the band gap in the all-inorganic perovskite $CsPbI_3$ from room to high temperatures

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AIMD simulation with the *NPT* ensemble

The AIMD simulations with the *NPT* ensemble are performed at γ-phase (400 K, 450 K), β-phase (500 K, 550 K), and α-phase (650 K, 700 K), respectively. The computational parameters are almost the same with those of *NVT* ensemble as description in main text. Differently, here the total simulation steps are 5000 and the timestep is 2 fs. After AIMD, the lattice parameters at *T* are the average values from the instantaneous configurations, the detial: from step 1000 to 3000 for 400 K, from step 1000 to 5000 for 450 K, 500 K, 550 K and 700 K, from step 1000 to 3500 for 650 K. After determining the lattice parameters , the atomic positions are further optimized.

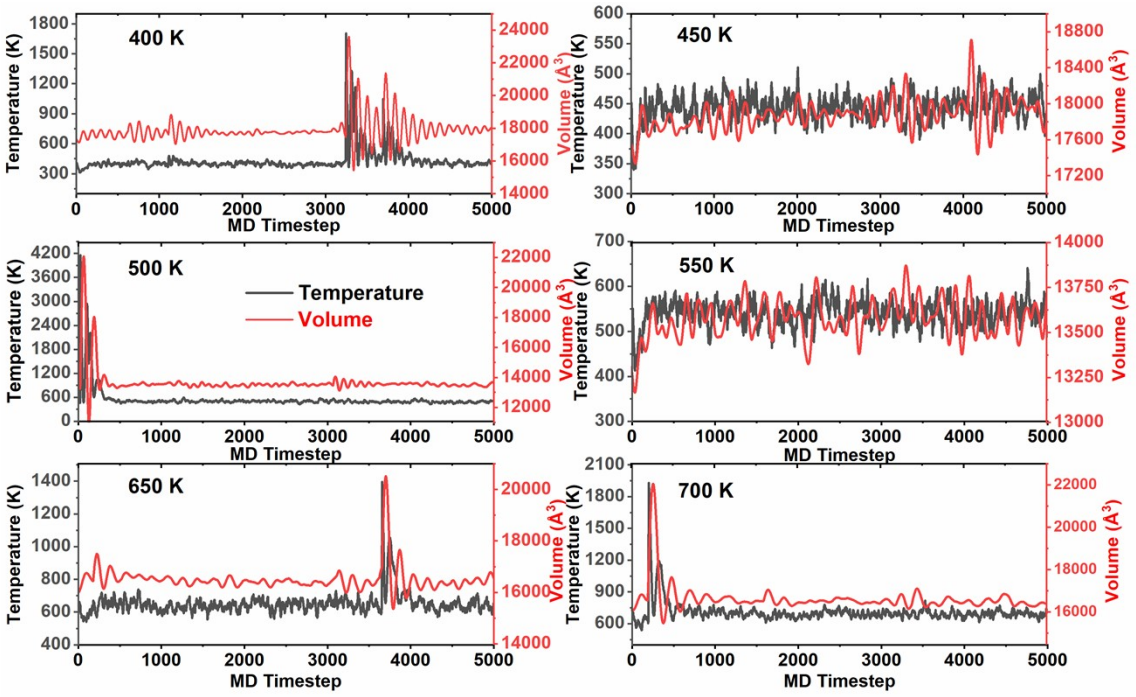

Figure S1. Temperature and volume as the functions of AIMD simulation (*NPT* ensemble) timestep with different preset temperatures in $CsPbI_3$.

Table S1. Lattice parameters (a_1, a_2, a_3 in Å and θ_1, θ_2, θ_3 in º), volume V (in Å^3), band gap E_g (in eV) from experiment (ACS Nano 2018, 12, 3477) and *NPT* AIMD sumlation for primitive cell $CsPbI_3$ at different phases and temperatures Ts (in K). The band gaps are calculated at the PBE level.

Phase	T	Experiment										*NPT* AIMD simulation									
		a_1	a_2	a_3	θ_1	θ_2	θ_3	V	$\frac{\Delta V}{V_0}$	E_g	ΔE_g	a_1	a_2	a_3	θ_1	θ_2	θ_3	V	$\frac{\Delta V}{V_0}$	E_g	ΔE_g
γ	400	8.71	8.82	12.54	90.00	90.00	90.00	964.08	0.0115	1.762	0.018	8.78	8.89	12.61	89.91	89.92	89.97	985.42	0.0099	1.817	0.028
	450	8.77	8.84	12.58	90.00	90.00	90.00	975.19		1.744		8.84	8.86	12.70	90.09	90.12	90.12	995.16		1.789	
β	500	8.83	8.83	6.30	90.00	90.00	90.00	490.78	0.0042	1.575	0.014	8.87	8.89	6.35	90.10	90.04	90.06	500.87	0.0060	1.604	0.015
	550	8.85	8.85	6.29	90.00	90.00	90.00	492.83		1.589		8.91	8.90	6.35	90.05	89.95	90.17	503.90		1.619	
α	650	6.30	6.30	6.30	90.00	90.00	90.00	249.64	0.0083	1.336	0.028	6.33	6.38	6.34	90.18	90.07	89.93	256.20	0.0072	1.387	0.035
	700	6.31	6.31	6.31	90.00	90.00	90.00	251.70		1.364		6.36	6.38	6.35	89.82	89.81	90.24	258.05		1.422	

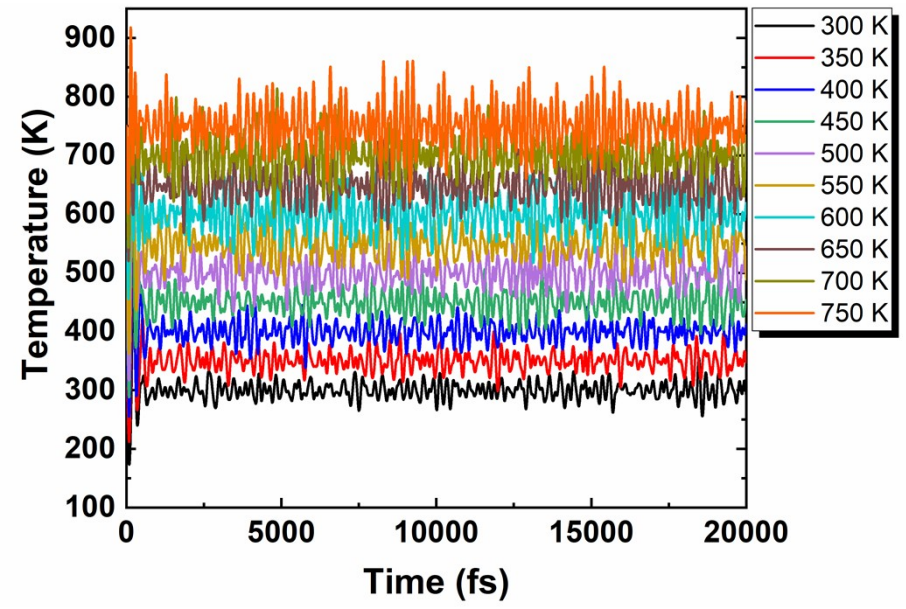

Figure S2. Temperature as the function of AIMD simulation (*NVT* ensemble) time with different preset temperatures in $CsPbI_3$.

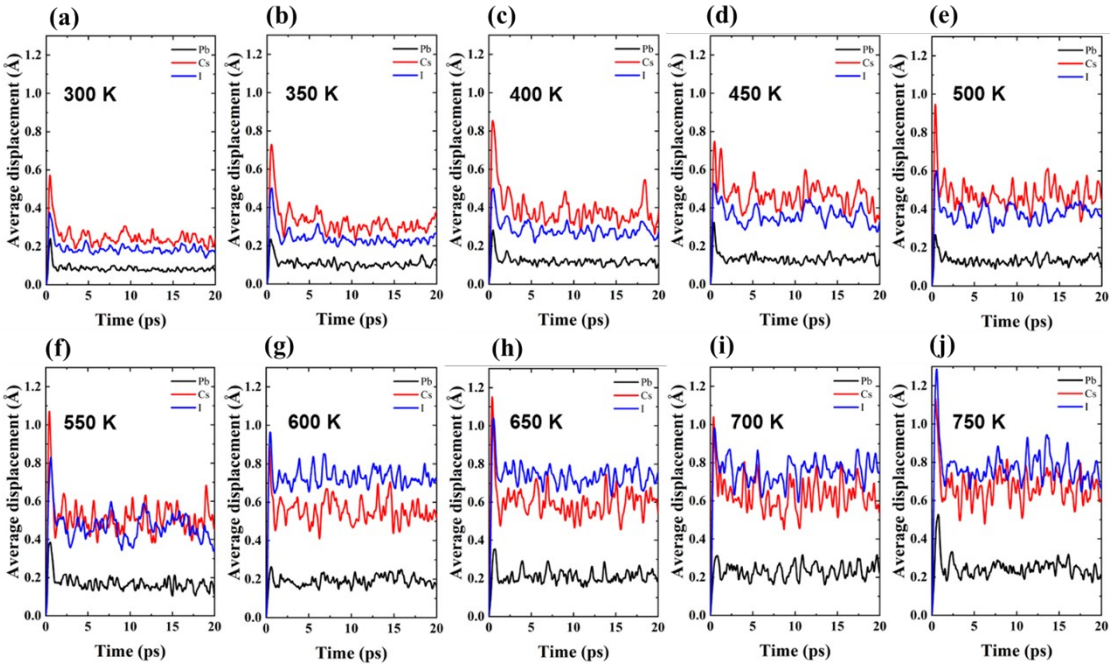

Figure S3. Atoms' average displacements as the function of AIMD simulation (*NVT* ensemble) time at different temperatures in $CsPbI_3$.

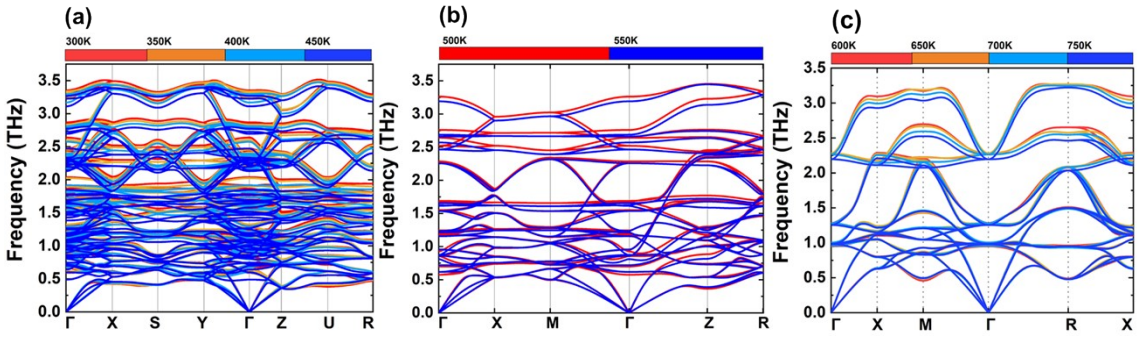

Figure S4. Phonon spectra at different temperatures of $CsPbI_3$ for (a) γ-phase, (b) β-phase and (c) α-phase.

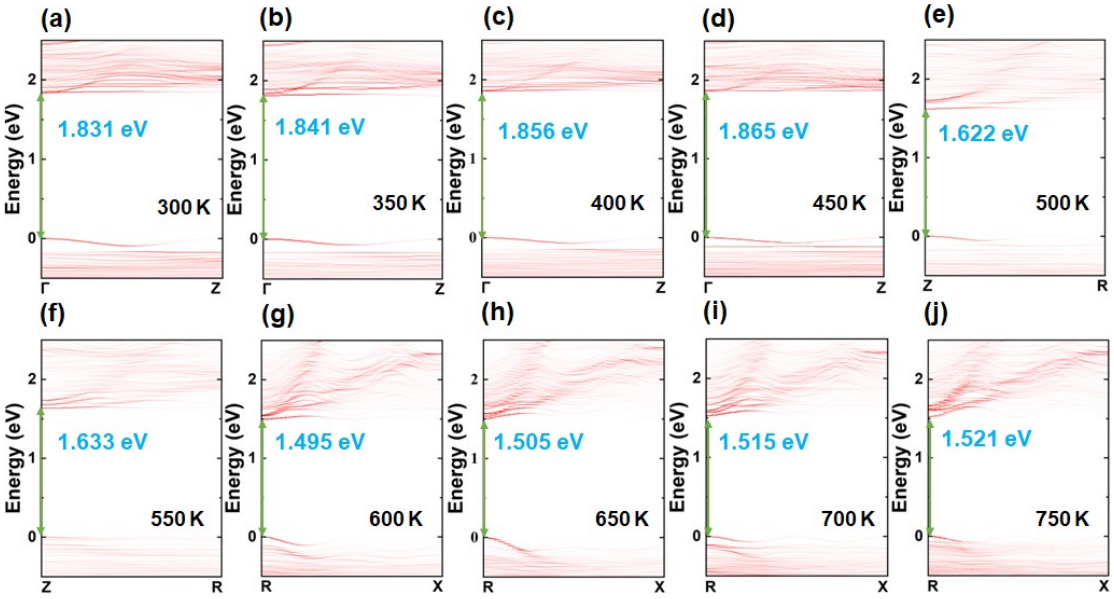

Figure S5. Effective band structures of $CsPbI_3$ with both considering the effects of lattice expansion and phonon vibrations at the PBE level. The energy of VBM is set as zero and the **k**-paths are **Γ** (0 0 0) – **Z** (0 0 0.5) for (a-d) γ-phase, **Z** (0 0 0.5) – **R** (0.5 0.5 0.5) for (e-f) β-phase, and **R** (0.5 0.5 0.5) – **X** (0 0.5 0) for (g-j) α-phase.

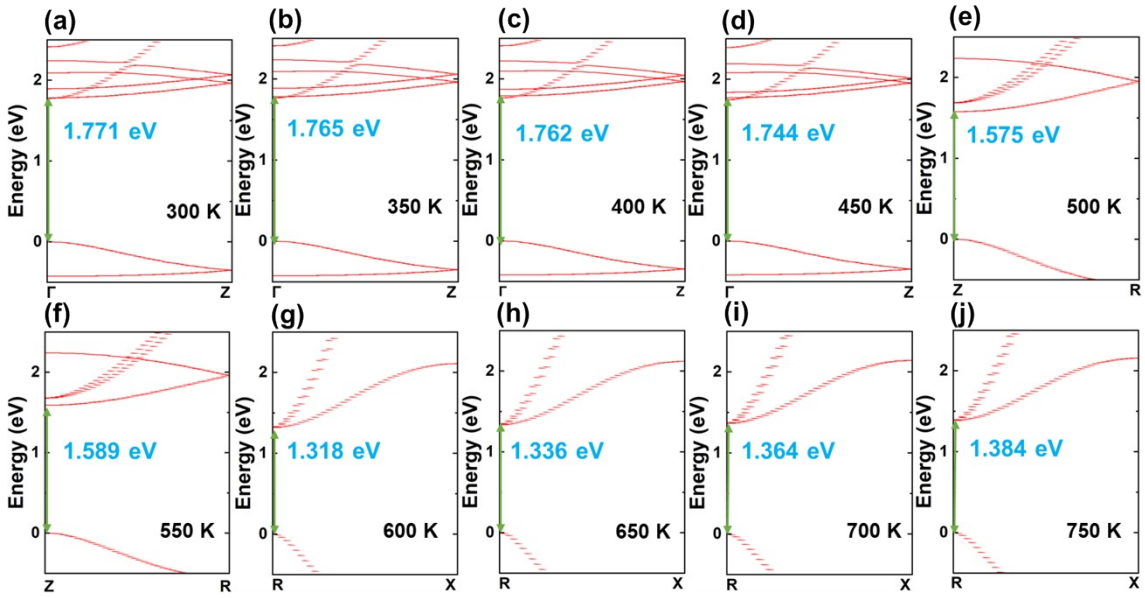

Figure S6. Band structures of $CsPbI_3$ with only considering the effect of lattice expansion at the PBE level. The energy of VBM is set as zero and the **k**-paths are **Γ** (0 0 0) – **Z** (0 0 0.5) for (a-d) γ-phase, **Z** (0 0 0.5) – **R** (0.5 0.5 0.5) for (e-f) β-phase, and **R** (0.5 0.5 0.5) – **X** (0 0.5 0) for (g-j) α-phase.

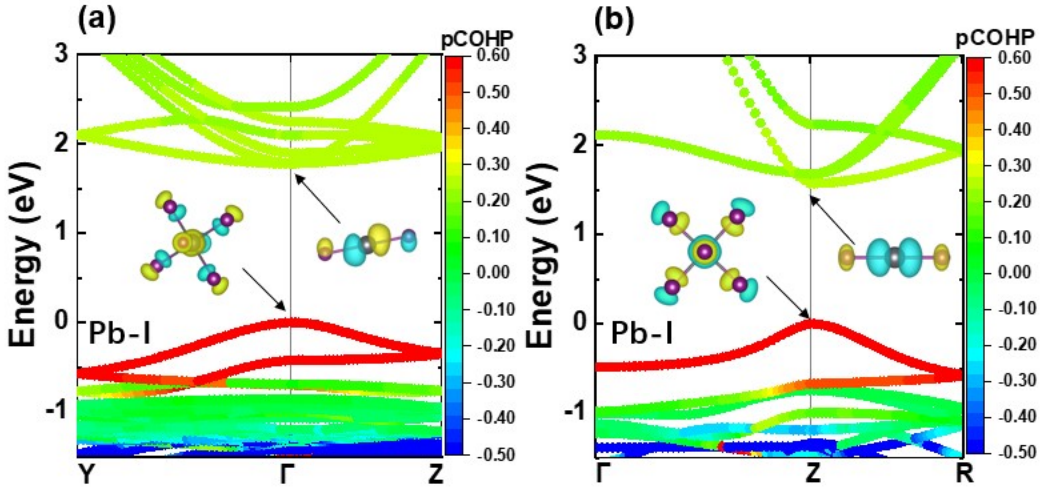

Figure S7. Band-resolved pCOHP analysis between Pb and I in the primitive cell of (a) γ-phase and (b) β-phase for $CsPbI_3$ at the PBE level. The VBM is set as zero and inset are the wavefunctions at CBM and VBM, respectively.

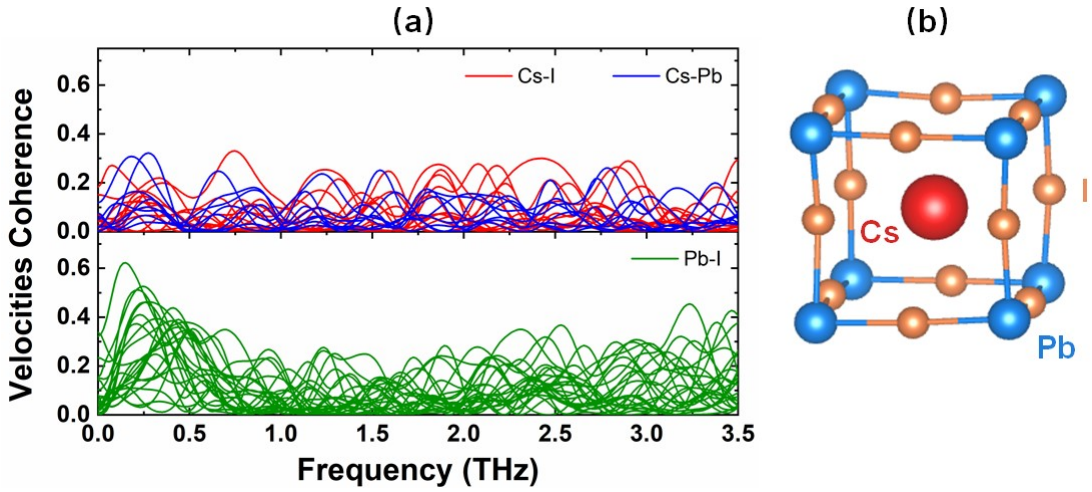

Figure S8. Velocity correlation functions (VCFs) as the function of frequency for the Cs and its near 12 I atoms (red lines), Cs and its near 8 Pb atoms (blue lines), as well as 24 Pb-I pairs (green lines). The VCFs are extracted from AIMD simulation (*NVT* ensemble) at 600 K of $CsPbI_3$'s supercell.

Table S2. Band gaps (in eV) of $CsPbI_3$ at different temperatures at the PBE and HSE levels, respectively. LE means only considering the effect of lattice expansion, and LE+VIB means both considering the effects of lattice expansion and phonon vibrations.

Temperature	LE		LE+VIB	
(K)	PBE (eV)	HSE (eV)	PBE (eV)	HSE (eV)
300	1.771	2.337	1.831	2.403
350	1.765	2.331	1.841	2.410
400	1.762	2.329	1.856	2.425
450	1.744	2.321	1.865	2.435
500	1.575	2.133	1.622 0.746*	2.176 1.203*
550	1.589	2.147	1.633	2.196
600	1.318	1.838	1.495	1.992
650	1.336	1.858	1.505	2.056
700	1.364	1.889	1.515	2.077
750	1.384	1.914	1.521	2.122

*Including the spin-orbit coupling (SOC) effect.

Table S3. Average values of Pb-I bond length and Pb-I-Pb bond angle for $CsPbI_3$ at different temperatures. LE means only considering the effect of lattice expansion, and LE+VIB means both considering the effects of lattice expansion and phonon vibrations.

Temperature	LE		LE+VIB	
(K)	Pb-I (Å)	Pb-I-Pb (˚)	Pb-I (Å)	Pb-I-Pb (˚)
300	3.1499	151.70	3.2255	149.85
350	3.2006	152.09	3.2272	150.15
400	3.2040	152.59	3.2354	150.27
450	3.2091	153.66	3.2357	151.60
500	3.1884	162.16	3.2170	157.11
550	3.1909	162.47	3.2201	157.21
600	3.1426	180	3.1888	163.54
650	3.1483	180	3.1959	163.47
700	3.1569	180	3.2067	163.25
750	3.1645	180	3.2184	162.84

*330 K, 370 K and 400 K for γ-phase; 500 K and 550 K for β-phase; 600 K, 650 K, 700 K and 750 K for α-phase.