Supporting Information for

Wurtzite-type $CuInSe_2$ for high-performance solar cells absorber: *ab* initio exploring the new phase structure

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Calculation methods

To find the stable structure at T=0 K, the lowest enthalpy of structure was used as the selected criterion in USPEX code. The first generation was produced randomly. Each subsequent generation was produced from the lowest-energy 60% of the previous generation. Among the new structures, 60% through heredity, 20% through permutation and 20% by lattice mutation were generated, respectively. In addition, the lowest energy structure of the previous generation survives into the next generation. The simulations would stop after 40 generations. After analyzing the results of evolutionary and optimizing the structures using VASP, many lowest-enthalpy structures were got. For the underlying first principles structural relaxations and electronic calculations, the plane-wave basis projector augmented wave (PAW) method in the framework of the density-functional theory within the generalized gradient approximation (GGA) as implemented in the VASP code was used. PBE, B3LYP, PBE plus U, and HSE06 XC functionals were employed, partially with van der Waals interaction. A planewave energy cutoff of 500 eV was used. The Brillouin zones k-point set (7×4×4) were sampled by Gamma centered grids which were chosen for wurtzite-type CIS. The electronic iterations convergence is 1.0E-08 eV. The lattice parameters and atomic positions are fully relaxed until the forces are smaller than 0.001eV/Å. For the phonon calculation, the calculation explores the full Brillouin zone and accounts for the interaction range of 10.0 Å. The asymmetric atoms are displaced by +/-0.02Å. The 3 × 3 × 2 supercell containing 96 atoms is used in such kind of calculations, the k-points set is 3 × 2 × 2.

Table S1. Energy differences for the different structures calculated by DFT-PBE. The energy is relative to the most stable structure, which is predicted in our current calculations. The positive value means that the structure is unstable relative to the new structure. The structure 1 and 2 are built based on the model proposed by Wang et al. (J. Am. Chem. Soc. 2010, 132, 12218–12221)

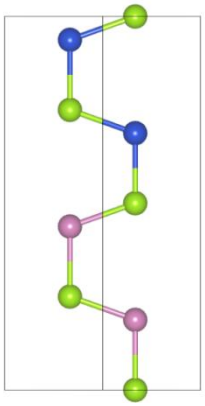
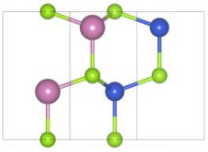
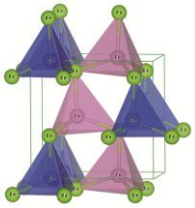
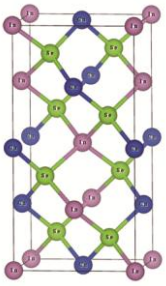
	Structure 1	**Structure 2**	**Our new structure**	**Common Chalcopyrite**
Atomic structure				
Relative energy difference per cell(8 atoms)	1.317 eV	0.489 eV	0 eV	-0.070 eV

Table S2. Space group, lattice constant, and fractional atomic positions of the wurtzite-type $CuInSe_2$ at HSE06 level.

Wurtzite $CuInSe_2$			
Spacegroup	$Pmc2_1$		
Spacegroup Number	26		
A (Å)	4.12454		
B (Å)	7.13556		
C (Å)	6.78608		
Alpha	90°		
Beta	90°		
gamma	90°		
Cu	0.00000	0.83214	0.49791
In	0.50000	0.66658	0.99674
Se1	0.00000	0.15146	0.35936
Se2	0.50000	0.68186	0.38148

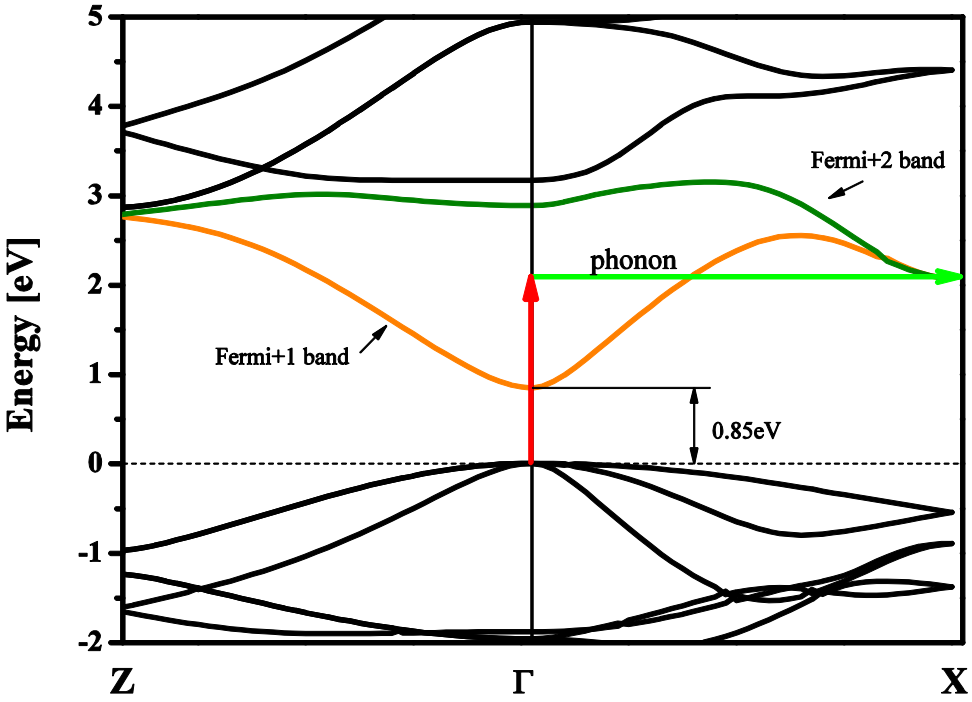


Fig. S1 The band structure of chalcopyrite $CuInSe_2$ with HSE06 functional. The second transition from G to X is also labeled out.

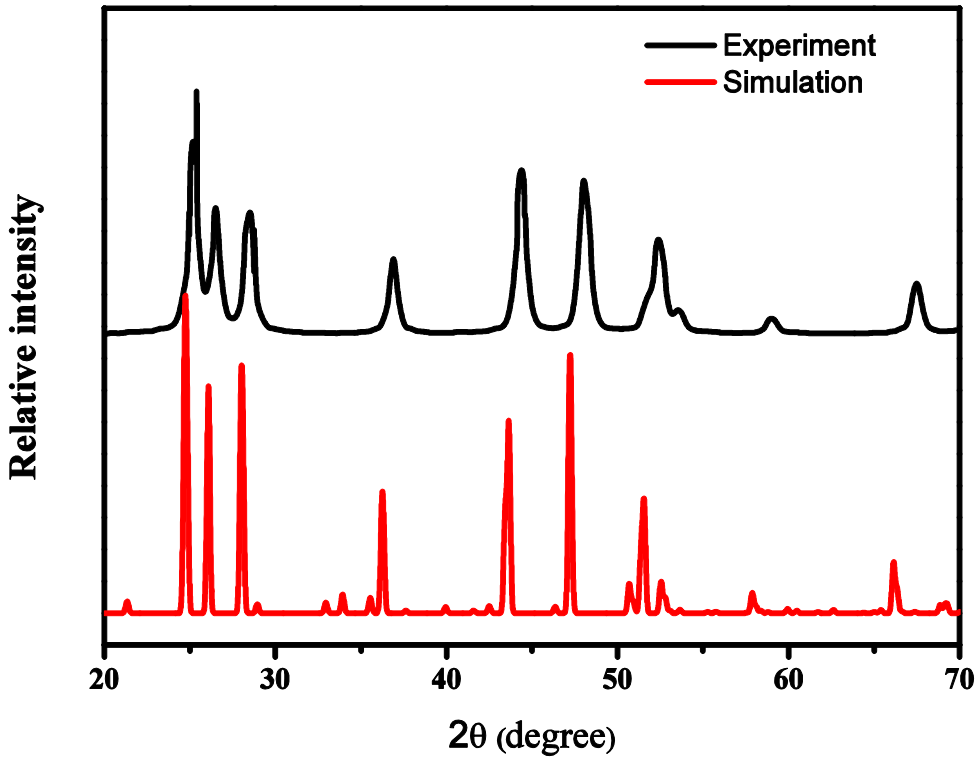


Fig. S2 Simulated XRD patterns with the predicted wurtzite-type structure ($Pmc2_1$) in comparison with the experimental result (J. Am. Chem. Soc. 2010, 132, 12218–12221.)

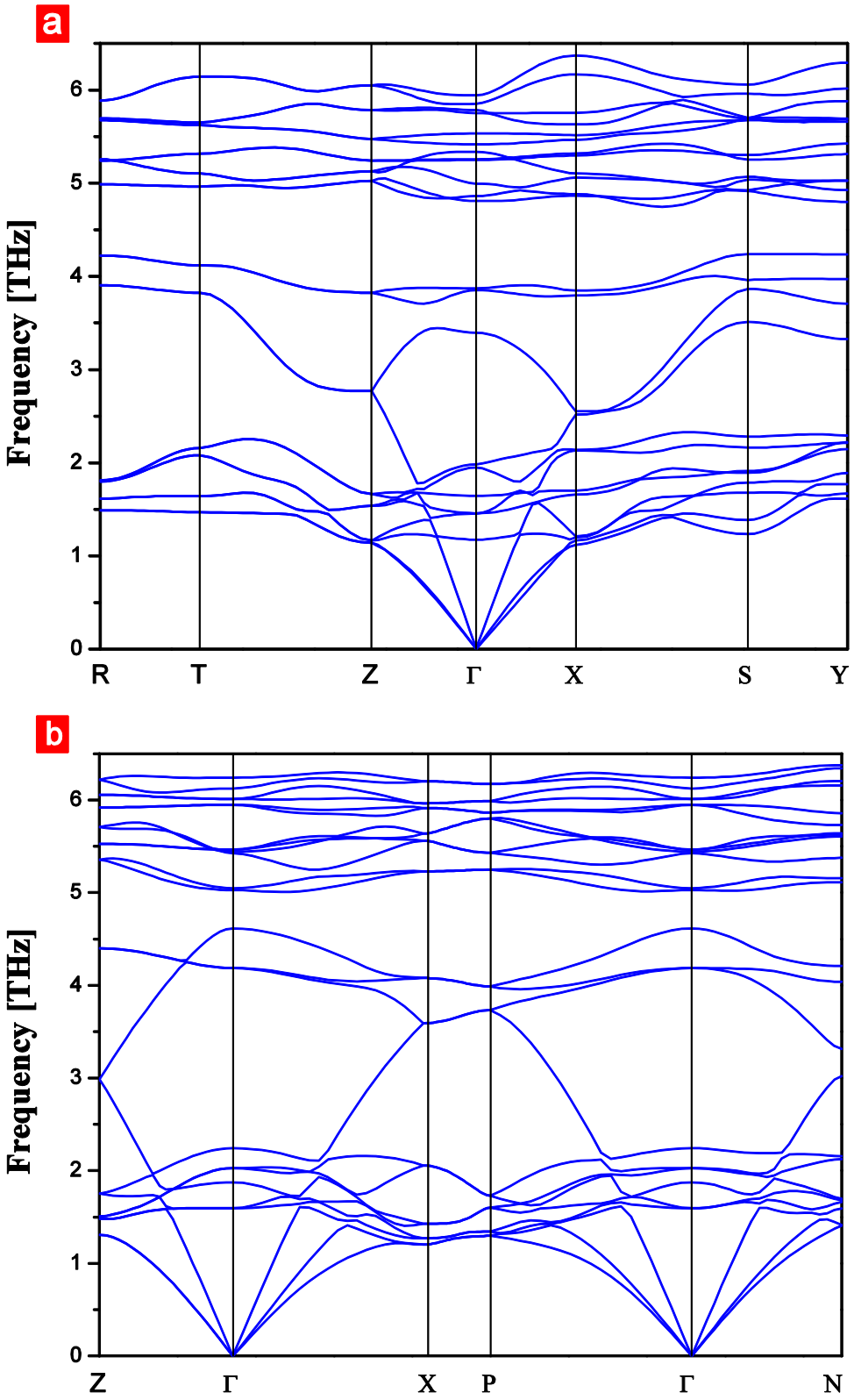


FIG. S3 Phonon dispersion relations of (a) wurtzite-type and (b) chalcopyrite CIS calculated with PBE functional.

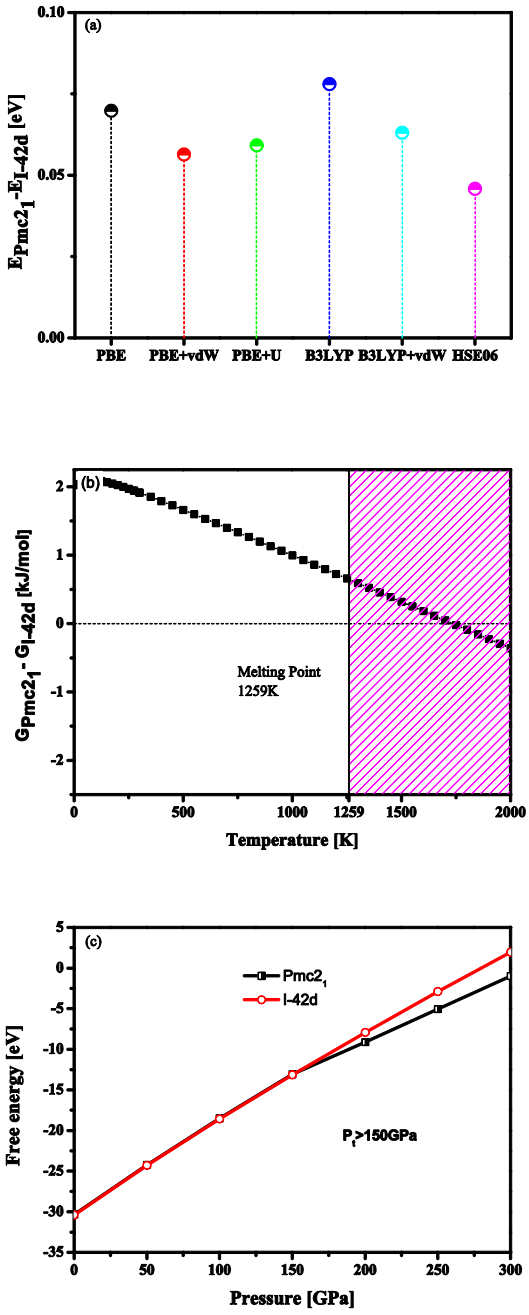


FIG. S4 (a) the energy difference between the wurtzite-type CIS and the chalcopyrite CIS at 0 K and 0 GPa, calculated with the difference functionals; (b) the Gibbs free energy difference between the wurtzite-type CIS and the chalcopyrite CIS at 0 Pa; (c) the Gibbs free energy difference at 0 K

between the predicted wurtzite-type and chalcopyrite structures of $CuInSe_2$. The positive value mean that the wurtzite-type CIS is less stable than the chalcopyrite CIS, vice versa.