Supplementary Material

Pressure-induced decomposition of solid hydrogen sulfide

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Computational details

Structure searching simulations through USPEX code were performed considering simulation sizes ranging from 1 to 4, 6, and 8 formula units per cell (f. u./cell) for H_2S and H_3S at pressures between 20 and 300 GPa. For the case of H_4S, H_5S and H_6S, the structure predictions are performed within 2 and 4 f. u. at pressures of 50, 100, 200 and 300 GPa. In the first generation, structures (population size: 10-60 structures, increasing with system size) are produced randomly. All produced structures were locally optimized at constant pressure and 0 K using the VASP code with energy cutoff of 500 eV and k-mesh of $2\pi\times0.05$ $Å^{-1}$. The subsequent generation is created from 60% of the lowest-enthalpy structures of the preceding generation by heredity (60%), permutation (10%), and lattice mutation (30%) operations. The best structure of each generation is also carried over to the next generation. The population size is set to at least twice the number of atoms in the cell. The calculation stops when the best structure does not change for more than 20 generations. Typically, the structure searching simulation for each calculation is stopped after we generate 1000~1200 structures (e.g., about 20~30 generations). Searching structures will cost much more computing time For example, H_3S at 200 GPa with four formula units, it will cost about seven days per twelve cores.

To analyze the results of searching structure, we select a number of distinct lowest-enthalpy structures and re-optimize their structures with higher accuracy as a function of pressures using VASP code. We used the 'hard' PAW potential of H and S with core radii of 0.8 and 1.5 a.u., respectively. The summation of the core radii of H and S is 2.3 a.u. or 1.217 Å, which is smaller than the H-S bond lengths in H_nS under the pressure range. It is safe to use such pseudopotentials in our studied pressure range. The Brillouin zone sampling using a grid spacing of $2\pi \times 0.03$ $Å^{-1}$ was individually adjusted in reciprocal space to the size of each computational cell and a plane-wave basis is set to 800 eV in all calculations. With such a choice the error bars of total energies are about 1 meV/atom. In the geometrical optimization, all forces on atoms were converged to less than 0.005 eV/Å. This process cost relatively little computing time than searching structures. For example, it takes about 34 hours per 12 cores to optimized the H_3S-*Cccm* structure from 10 GPa to 300 GPa.

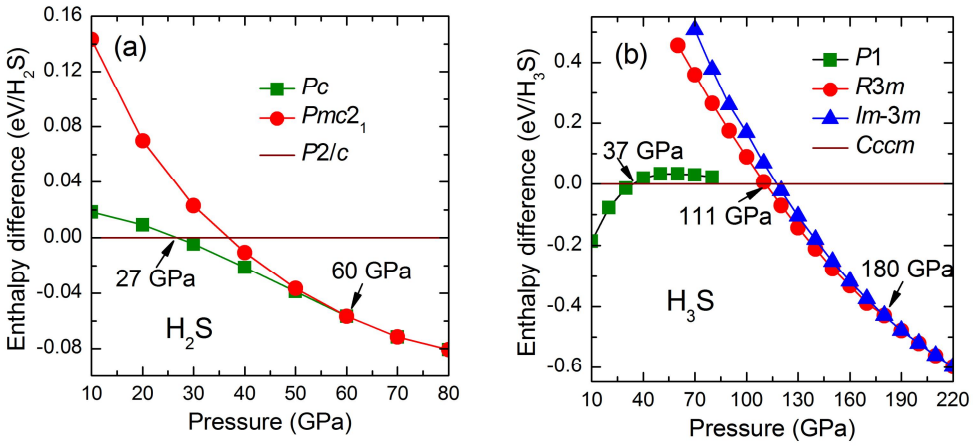

FIG. S1 (Color online) (a) Calculated enthalpy differences of *P*2/*c*, *Pc* and *Pmc*2$_1$ phases in H_2S (relative to the *P*2/*c* phase) as functions of pressure. (b) Calculated enthalpy differences of *P*1, *Cccm*, *R*3*m* and *Im*-3*m* phases in H_3S (relative to the *Cccm* phase) as functions of pressure.

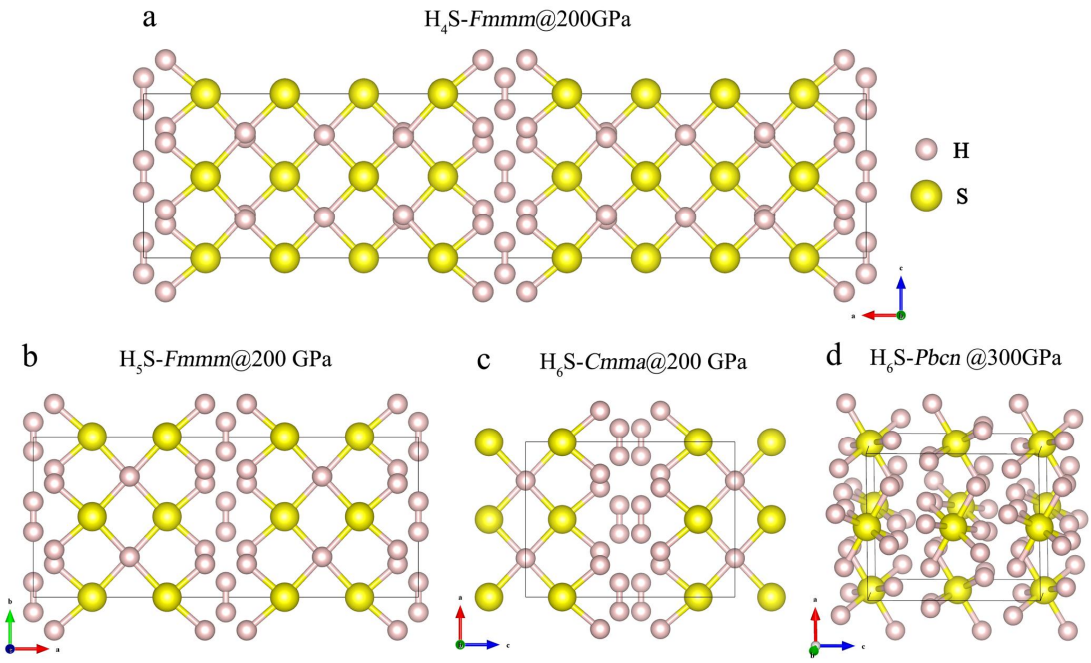

FIG. S2. (Color online) Selected metastable structures of H_4S, H_5S and H_6S stoichiometries. a, H_4S at 200 GPa in a *Fmmm* structure. b, H_4S at 200 GPa in a *Fmmm* structure. c, H_6S at 200 GPa in a *Cmma* structure. d, H_6S at 300 GPa in a *Pbcn* structure. Large yellow spheres represent S and small pink spheres denote H atoms, respectively.