Supplementary Information:

Novel Superconducting Electrides in Ca–S System under High Pressures

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Computational Details

We have explored the pressure-induced structural evolution in Ca–S system with various Ca_mS_n (m = n = 1-4) using the CALYPSO and USPEX codes with simulation cell sizes of 1-4 formula units (f.u.) at temperature of 0 K and pressures at 0, 50, 100, 150 and 200 GPa. Such methods have been successfully employed in various systems. The CALYPSO structure searching: In the first step, random structures with certain symmetry are constructed in which atomic coordinates are generated by the crystallographic symmetry operations. After processing the first generation structures, 60% of them with lower Gibbs free energies are selected to construct the next generation structures by PSO (Particle Swarm Optimization). 40% of the structures in the new generation are randomly generated. A structure fingerprinting technique of bond characterization matrix is applied to the generated structures, so that identical structures are strictly forbidden. The energy convergence was set to 10-5 eV. The USPEX structure searching: In the evolutionary structural searching, the first generation of structures was always created randomly with its population size of 20-60 structures. The succeeding generations are produced by variation operator heredity (60%), lattice mutation (30%) and permutation (10%).

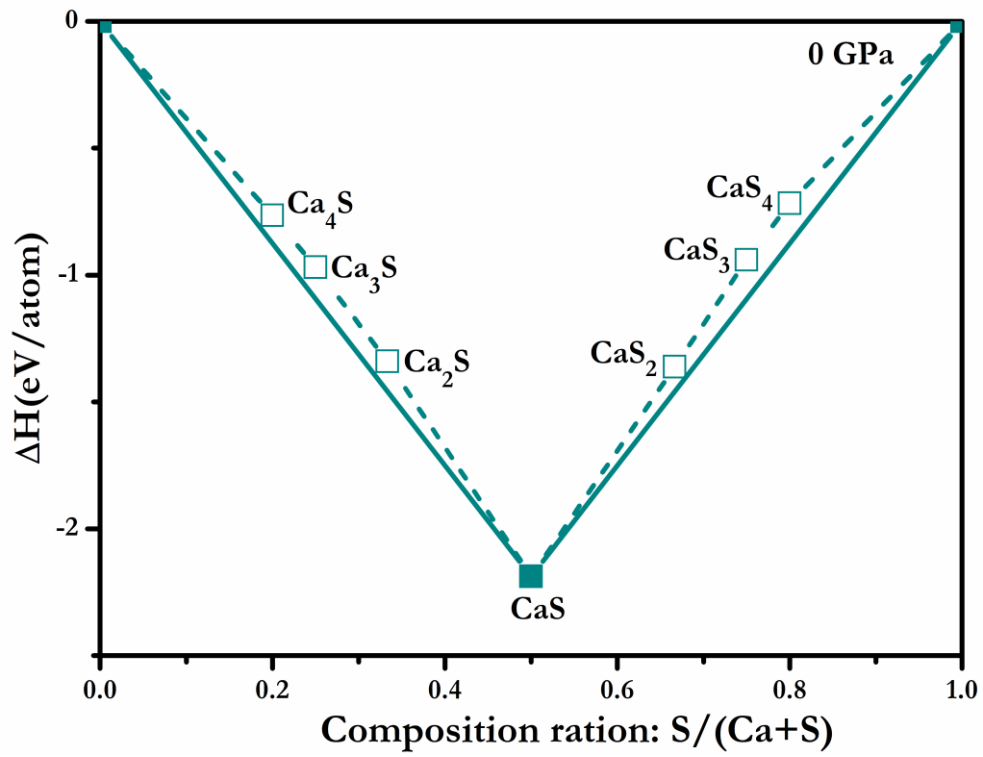

Figure S1. Calculated formation enthalpies of various Ca−S compounds at 0 GPa.

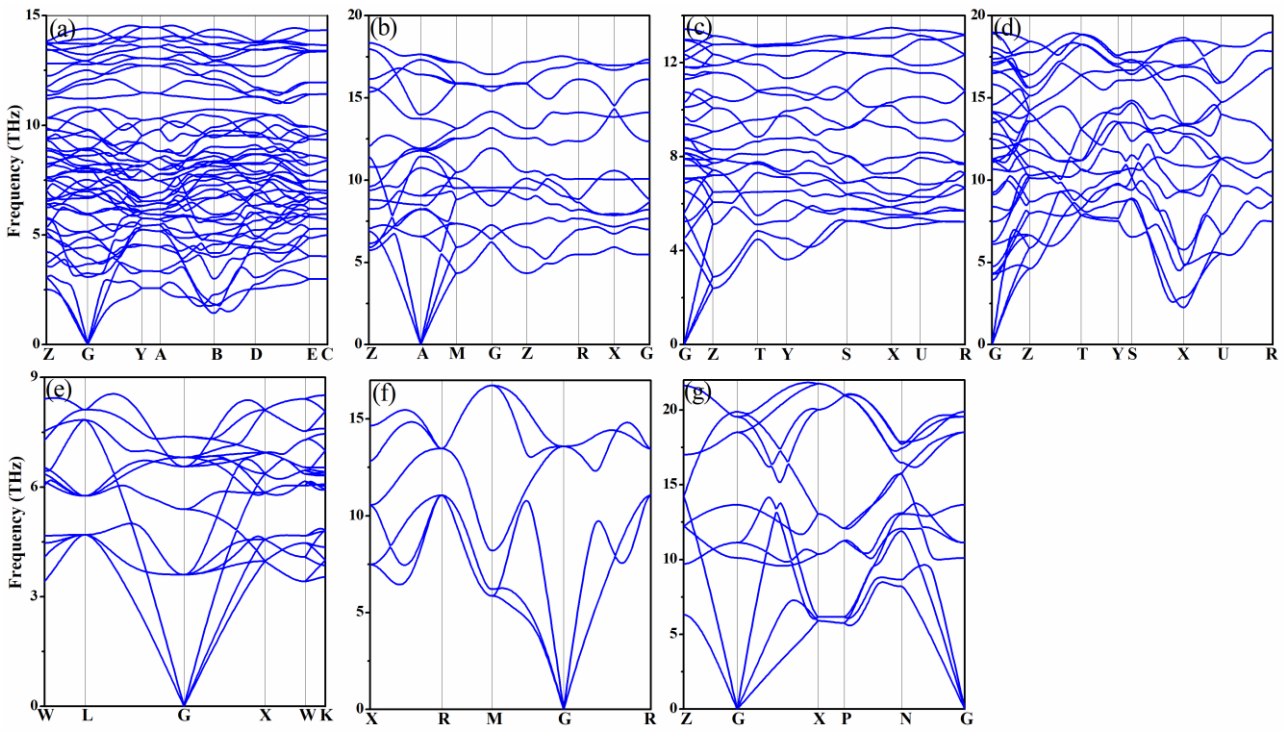

Figure S2. The calculated phonon spectra of the predicted stable Ca-rich compounds at selected pressures. (a) $P2_1/m$ Ca_3S at 60 GPa (b) $P4/mbm$ Ca_3S at 150 GPa (c) *Pnma* Ca_2S at 50 GPa (d) *Cmcm* Ca_2S at 150 GPa (e) *Fm*-3*m* CaS at 0 GPa (f) *Pm*-3*m* CaS at 100 GPa (g) $I4_1/amd$ CaS at 200 GPa.

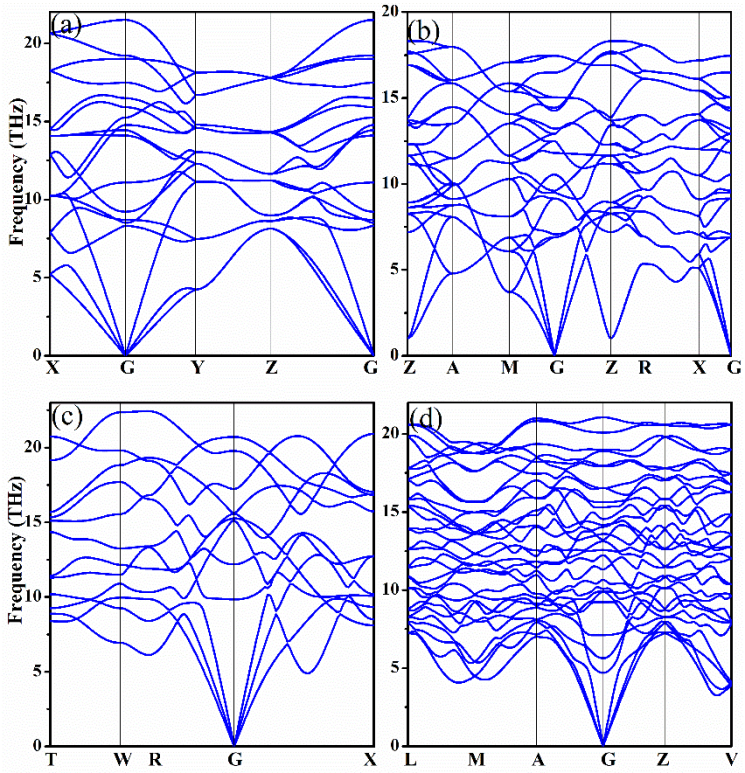

Figure S3. The calculated phonon spectra of the predicted stable S-rich compounds at selected pressures. (a) *Fddd* CaS_2 at 150 GPa (b) *P*-42_1m CaS_3 at 100 GPa (c) *Immm* CaS_3 at 200 GPa (d) *C*2/*c* CaS_4 at 200 GPa.

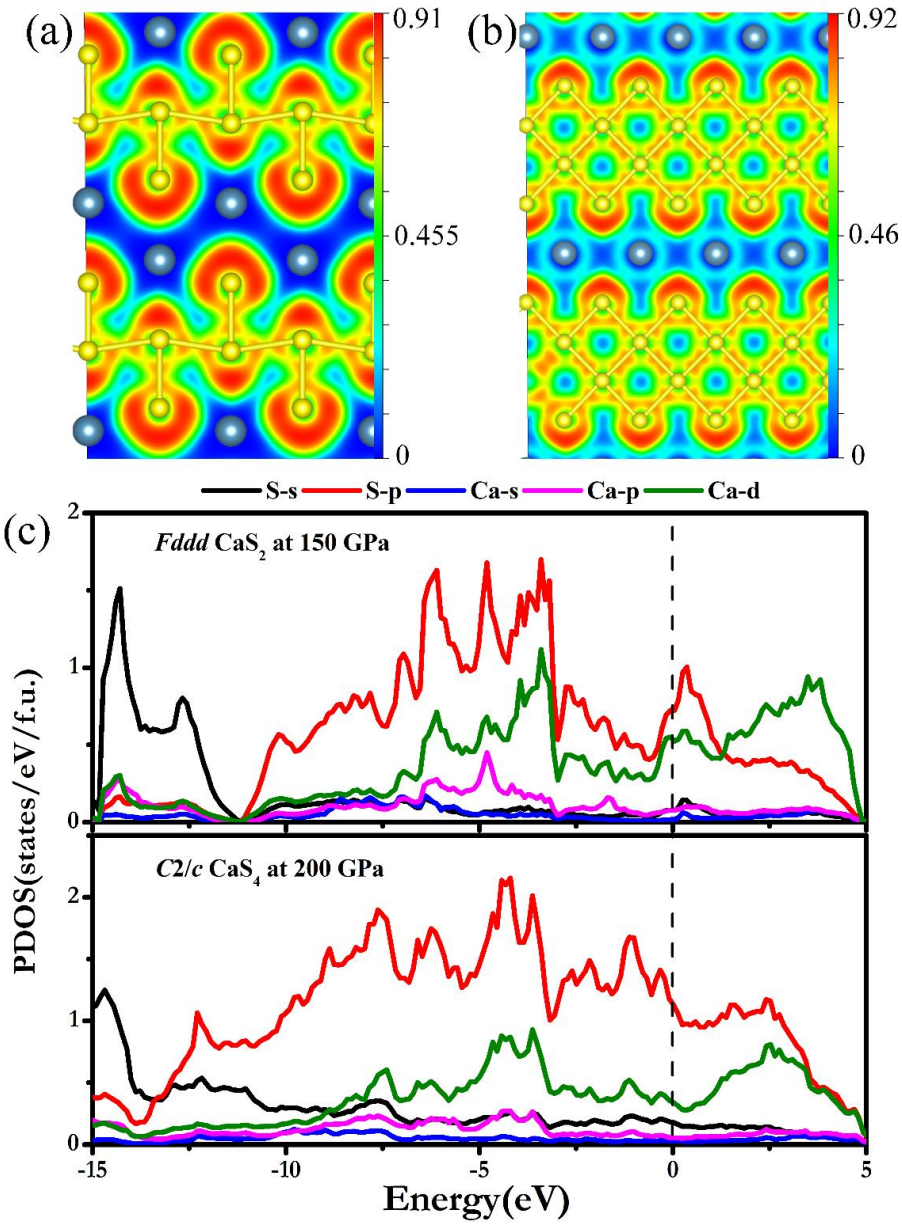

Figure S4. The calculated electron localization function (ELF) for CaS_2 and CaS_4. (a) *Fddd* CaS_2 (b) *C*2/*c* CaS_4 and (c) projected density of states (PDOS) for CaS_2 and CaS_4.

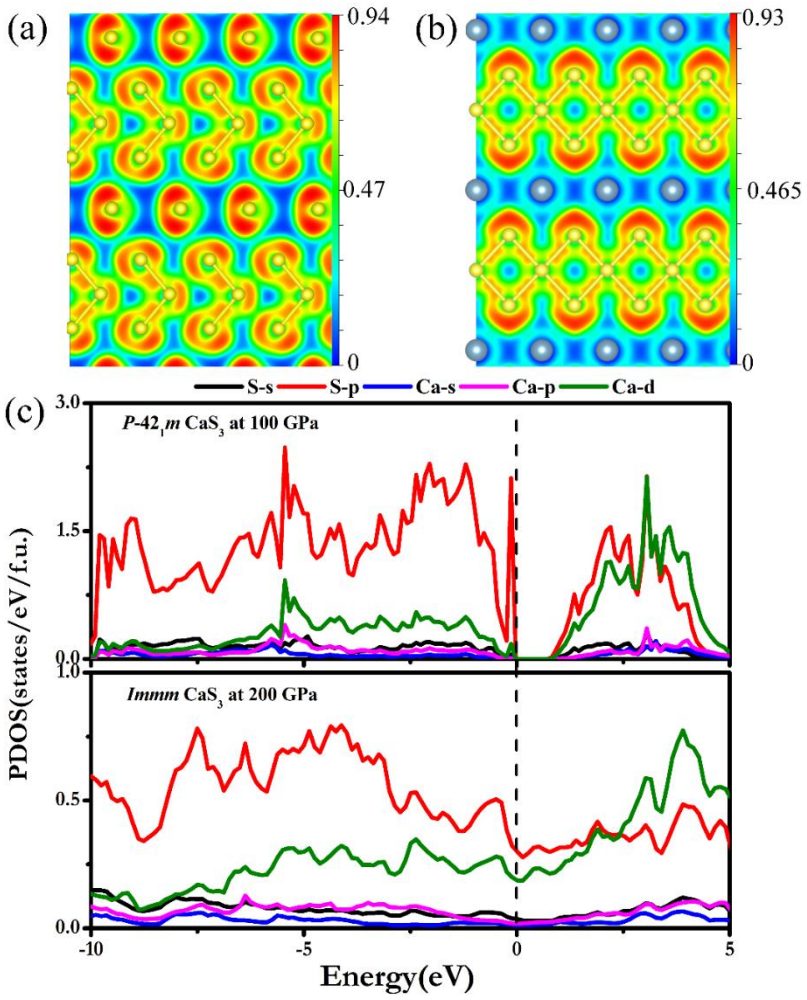

Figure S5. The calculated electron localization function (ELF) for CaS_3. (a) *P*-42_1m (b) *Immm* and (c) projected density of states (PDOS) for CaS_3.

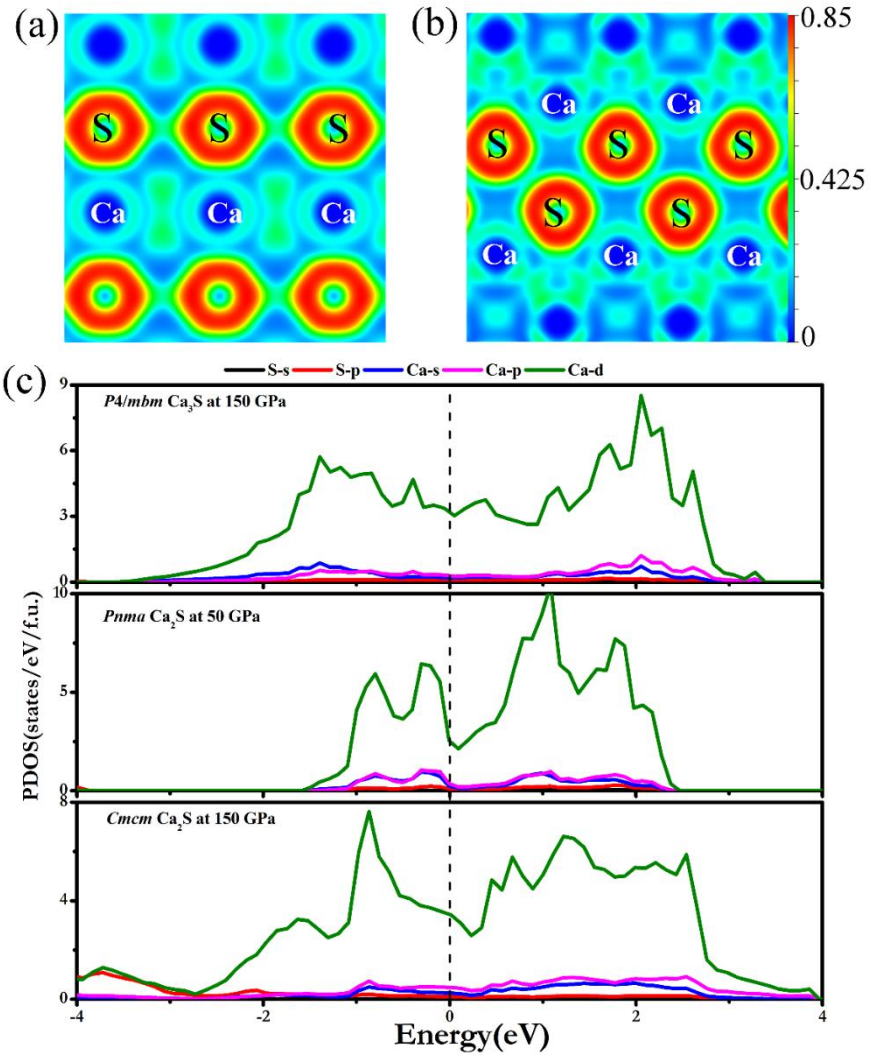

Figure S6. The calculated electron localization function (ELF). (a) *P*4/*mbm* Ca_3S (b) *Cmcm* Ca_2S and (c) projected density of states (PDOS) of *P*4/*mbm* Ca_3S, *Pnma* Ca_2S and *Cmcm* Ca_2S.

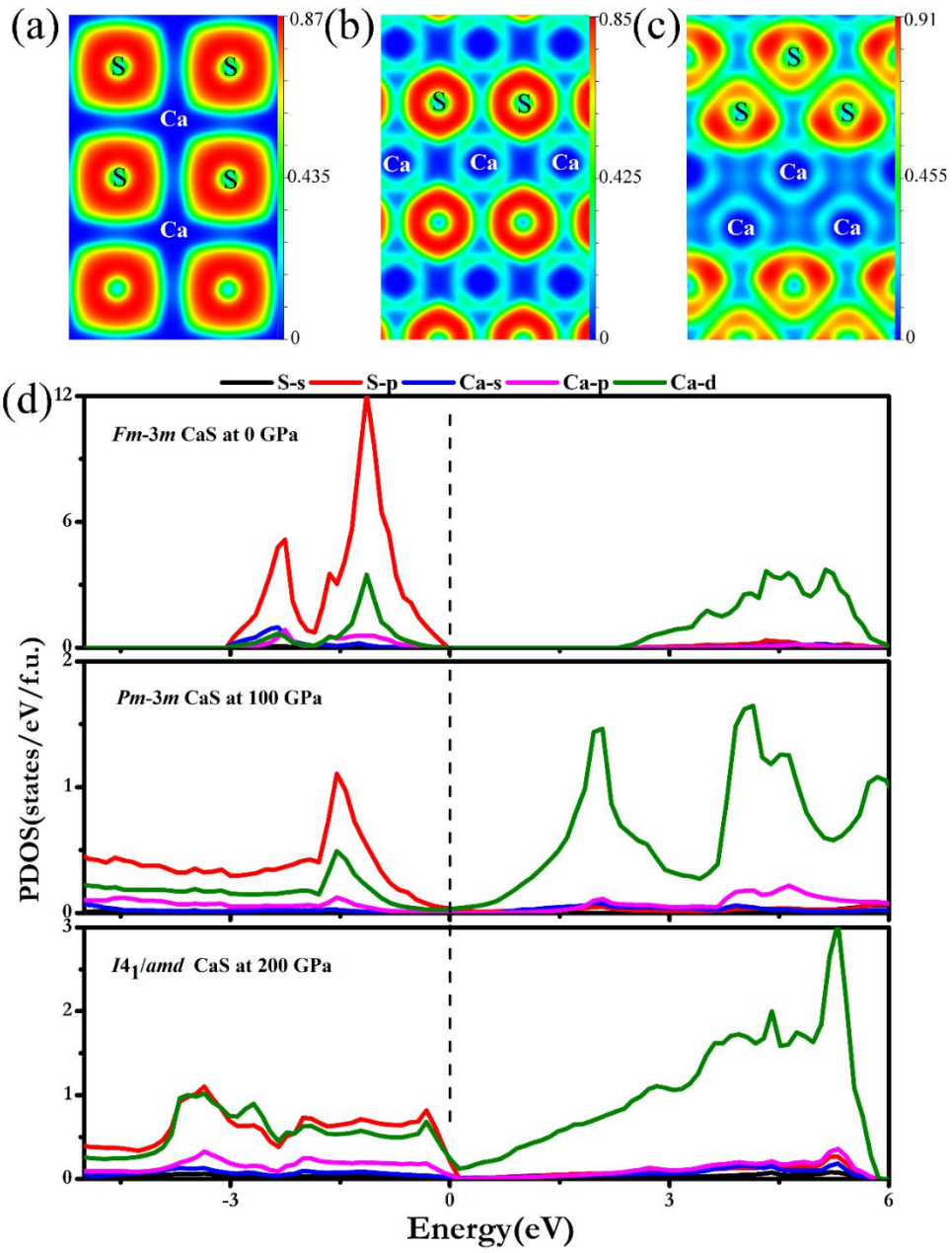

Figure S7. The calculated electron localization function (ELF) for CaS. (a) *Fm*-3*m* (b) *Pm*-3*m* (c) $I4_1/amd$ and (d) projected density of states (PDOS) for CaS.

Table S1 Structural parameters of Ca-S system at selected pressure.

Space group pressure	Lattice parameters (Å, °)	Atomic coordinates (fractional)	Sites
*P*2$_1$/*m* Ca_3S 50 GPa	a=11.7601 b=3.9581 c=5.2798 α=γ=90 β=95.413	Ca1 0.71746 0.75000 0.43627 Ca2 0.81856 0.25000 0.25522 Ca3 0.46173 0.75000 0.31037 Ca4 0.36082 0.25000 0.06974 Ca5 0.11197 0.25000 0.11684 Ca6 0.01756 0.75000 0.32048 S1 0.23980 0.75000 0.25497 S2 0.59000 0.25000 0.21484	2e 2e 2e 2e 2e 2e 2e 2e
*P*4/*mbm* Ca_3S 200 GPa	a=b=4.8148 c=3.2719 α=β=γ= 90	Ca1 0.30036 -0.80036 0.00000 Ca3 0.00000 -0.50000 -1.50000 S1 0.50000 -0.50000 -1.50000	4g 2c 2b
Pnma Ca_2S 100 GPa	a=4.9357 b=3.7499 c=7.8553 α=β=γ=90	Ca1 0.80971 0.25000 0.55808 Ca3 0.79889 0.25000 0.87482 S1 1.10750 0.75000 0.80442	4c 4c 4c
Cmcm Ca_2S 200 GPa	a=2.7546 b=10.6536 c=3.8931 α=β=γ= 90	Ca1 0.50000 0.22561 0.75000 Ca2 0.50000 0.42441 1.25000 S1 -0.00000 0.40158 0.75000	4c 4c 4c
Fm-3*m* CaS 0 GPa	a=b=c=5.7101 α=β=γ=90	Ca1 0.50000 0.50000 1.00000 S1 0.50000 0.50000 0.50000	4a 4b
Fm-3*m* CaS 100GPa	a=b=c=2.90180 α=β=γ=90	Ca1 -1.50000 -1.50000 -0.50000 S1 -1.00000 -1.00000 -1.00000	1b 1a
*I*4$_1$/*amd* CaS 200 GPa	a=b=3.3034 c=7.0815 α=β=γ= 90	Ca1 -1.00000 1.50000 0.25000 S1 -1.50000 0.50000 0.00000	4a 4b
Fddd CaS_2 200 GPa	a=7.4559 b=4.3278 c=6.8838 α=β=γ= 90	Ca1 0.75000 0.75000 0.25000 S1 0.25000 0.75000 0.10063	8a 16g
P-42$_1$*m* CaS_3 100 GPa	a=b=5.4158 c=3.0567 α=β=γ=90	Ca1 0.00000 -0.00000 -0.50000 S1 0.50000 -0.00000 -0.41780 S3 0.20088 0.70088 -0.99872	2b 2c 4e
Immm CaS_3 200 GPa	a=6.7265 b=3.8997 c=2.734 α=β=γ= 90	Ca1 -0.50000 -0.50000 -0.50000 S1 -0.21893 -0.50000 -0.00000 S9 -0.50000 -1.00000 -0.00000	2a 4f 2b
*C*2/*c* CaS_4 200 GPa	a=7.97428 b=2.86929 c=11.95417 α=γ=90 β=139.9	Ca1 0.00000 0.49966 0.75000 Ca2 0.50000 0.99966 0.75000 Ca3 0.00000 0.50034 0.25000 Ca4 0.50000 0.00034 0.25000 S1 0.88316 0.00020 0.33897 S2 0.66275 0.00030 0.01903 S3 0.38316 0.50020 0.33897	1a 1a 1a 1a 1a 1a 1a

		S4 0.16275 0.50030 0.01903 S5 0.11684 0.00020 0.16103 S6 0.33725 0.00030 0.48097 S7 0.61684 0.50020 0.16103 S8 0.83725 0.50030 0.48097 S9 0.11684 0.99980 0.66103 S10 0.33725 0.99970 0.98097 S11 0.61684 0.49980 0.66103 S12 0.83725 0.49970 0.98097 S13 0.88316 0.99980 0.83897 S14 0.66275 0.99970 0.51903 S15 0.38316 0.49980 0.83897 S16 0.16275 0.49970 0.51903	1a 1a 1a 1a 1a 1a 1a 1a 1a 1a 1a 1a 1a