

Supplementary Online Materials: Formation of Stoichiometric CsF_n Compounds

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I. STABILITY OF CsF UNDER PRESSURE

Our detailed variable-composition structure searches between CsF and F, implicitly assume that CsF should be stable at all pressures. To check this, we also performed structure searches with up to 20 atoms for the entire composition space between Cs and F at 0 and 100 GPa, respectively. As shown in Fig. S1, we found that (1) CsF is stable at both ranges; (2) most of the new stoichiometries are located between CsF and F. This assures that our search strategy is correct.

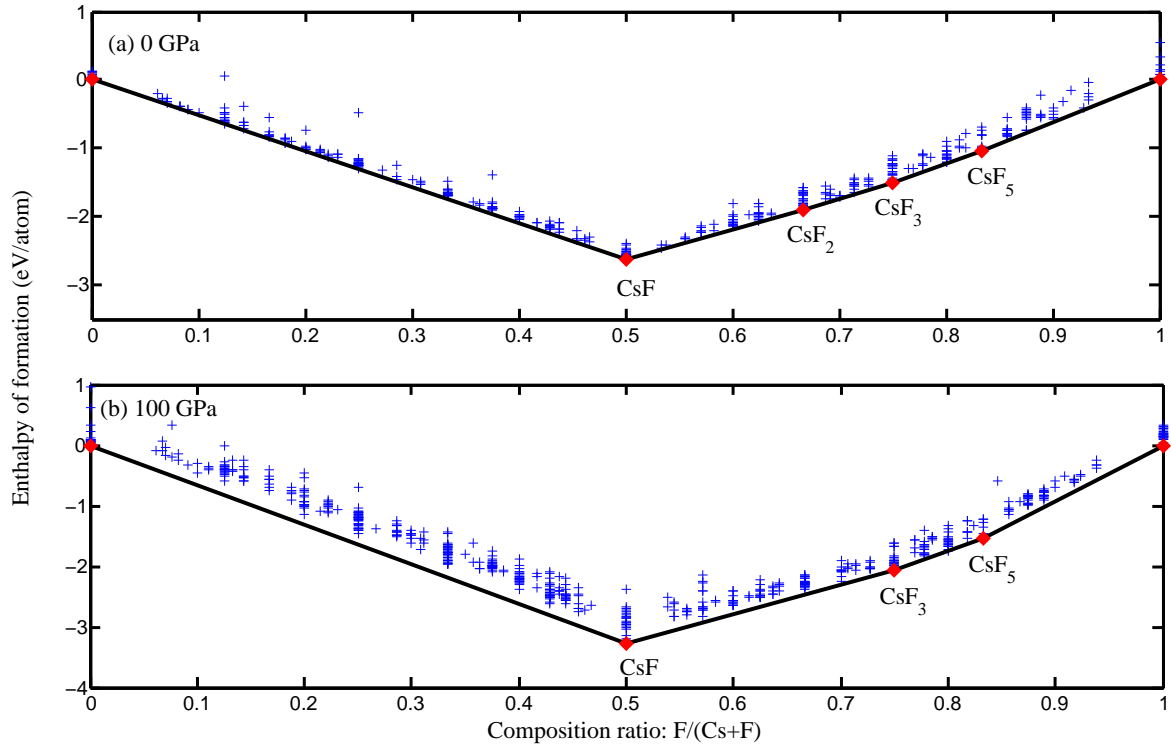


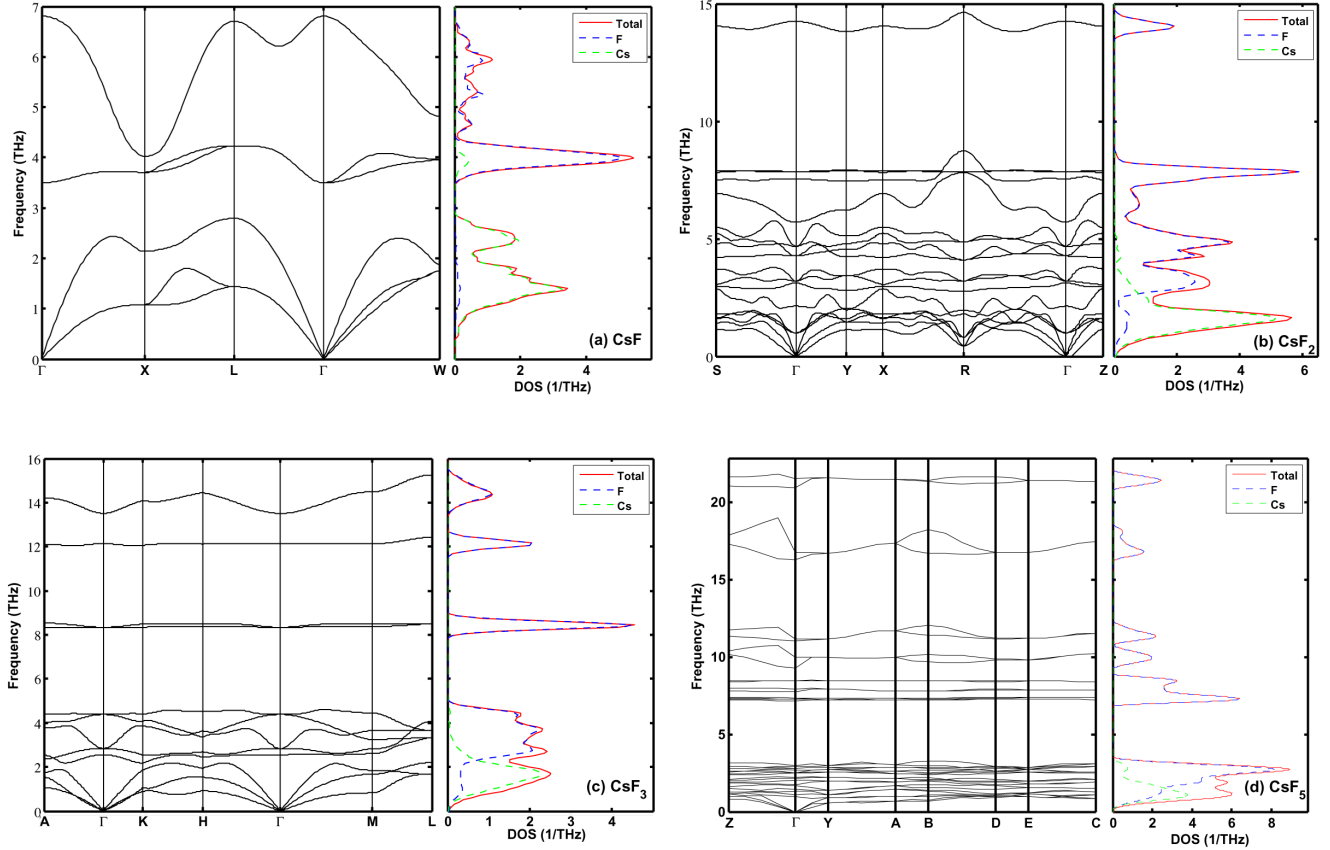
FIG. S1. Relatively stabilities for all compounds in the Cs-F system at (a) 0 GPa; and (b) 100 GPa, respectively.

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23 II. VIBRATIONS AND THERMODYNAMICS OF CsF_n AT AMBIENT PRESSURE

24 A. Free energy of solids

25 The calculated vibrational behaviors for CsF_n ($n=1,2,3,5$) compounds under ambient pressures are given in Fig.
 26 S2. All of the dispersion curves have no imaginary phonon frequencies, indicating that they are all dynamically stable.
 27 The phonon densities of states were also calculated using a $10 \times 10 \times 10$ grid of wave vectors.



28

29 FIG. S2. Calculated phonon dispersion and density of states of (a) $Fm\bar{3}m$ - CsF ; (b) $I4/mmm$ - CsF_2 ; (c) $R\bar{3}m$ - CsF_3 ; (d)
 30 $P2_1$ - CsF_5 at ambient pressure.
 31

32 The free energy of solid (such as CsF_n compounds), can be expressed as,
 33

$$G(T, V) = U(V) + F_{\text{elec}} + F_{\text{vib}}, \quad (1)$$

34 where U is the internal lattice energy, while F_{elec} and F_{vib} denote the electronic and vibrational contributions. The
 35 electronic excitations are usually neglected, while vibrational contributions represents the phonon energy, which can
 36 be treated in the harmonic approximation, by summing over the normal modes frequencies,

$$F_{\text{vib}} = \frac{1}{2} \sum_{i=1}^n hv_i \left[\frac{1}{2} + \frac{1}{\exp(-hv_i/kT) - 1} \right], \quad (2)$$

37 where k is Boltzmann constant, h is Planck constant.

38 B. Free energy of F₂ gas

39 On the other hand, the free energy of diatomic F₂ gas molecule can be expressed as:

$$G(\text{F}_2) = U(\text{F}_2) + \frac{7}{2}k_B T - TS(\text{F}_2), \quad (3)$$

40 where the entropy S can be divided into three parts, namely, translation entropy S_{trans} , rotational entropy S_{rot} ,
41 vibrational entropy S_{vib} and electronic entropy S_{elec} . Again, S_{elec} is neglected, while the other terms can be defined
42 as,

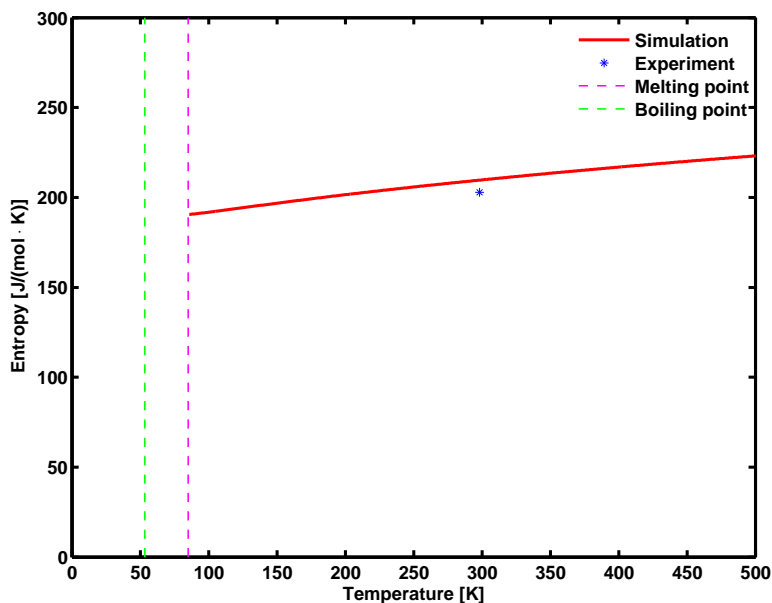
$$\begin{aligned} S_{\text{trans}} &= \frac{5}{2}Nk + Nk \ln \left[\frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right], \\ S_{\text{rot}} &= Nk + Nk \ln \frac{T}{2\Theta_{\text{rot}}}, \\ S_{\text{vib}} &= \frac{Nk\Theta_{\text{vib}} \left(\frac{1}{2} + \frac{1}{\exp(\Theta_{\text{vib}}/T) - 1} \right)}{T} + Nk \ln \left(\frac{\exp(-\Theta_{\text{vib}}/T)}{1 - \exp(-\Theta_{\text{vib}}/T)} \right). \end{aligned} \quad (4)$$

43 Here, Θ_{rot} and Θ_{vib} are the characteristic rotational and vibrational temperatures, respectively.

$$\begin{aligned} \Theta_{\text{rot}} &= \frac{(h/2\pi)^2}{2kI}, \\ \Theta_{\text{vib}} &= \frac{hv}{k}, \end{aligned} \quad (5)$$

44 where I is a molecular moment of inertia, v is the vibration frequency of F₂ molecule. To be consistent with the free
45 energy calculation of solids, here we calculated the entropy of F₂ within the same functional. The relaxed F-F bond
46 length in F₂ molecule is 1.43 Å, in satisfactory agreement with the experimental report (1.42 Å). The theoretical
47 vibrational frequency for F-F stretching modes of F₂ is 30.1 THz, compared with the experimental value 27.489 THz.
48 Note that the vibrational component of the gas entropy here is very small (less than 10% of the total).

49 The calculated temperature dependent $S(\text{F}_2)$ is shown in Fig. S3. Compared to the experimental value ($S^{\text{expt}}(\text{F}_2)$
50 = 202.8 J/(mol · K)) at standard conditions, our results are close.



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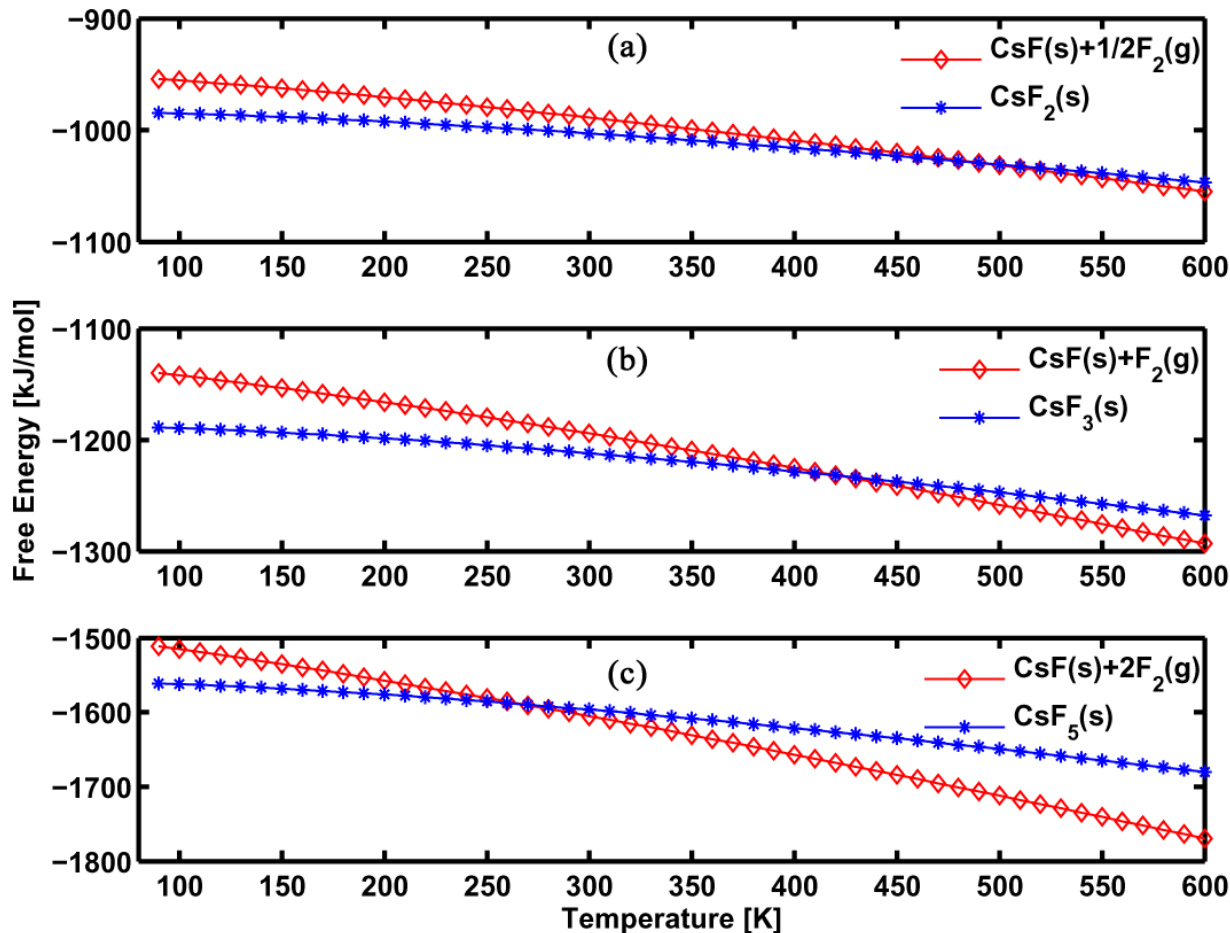
52 FIG. S3. The calculated entropy of F₂ gas at different temperatures. The melting point (53.48 K) and boiling point (85.03
53 K) are also shown for being consistent.

54

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56 C. Thermochemistry of the suggested reactions

57 By applying the eq. 1 and eq. 3, we obtain the formation energy of the suggested chemical reactions in Table 1.
 58 The results are shown in S4. And the predicted decomposition temperatures are 491 K for CsF₂, 423 K for CsF₃,
 59 and 258 K for CsF₅, respectively. All of these temperatures are easily accessible, thus these materials are promising
 60 for reversible fluorine storage materials.



61
 62 FIG. S4. The temperature dependence of free energy of the suggested chemical reactions (a) $\text{CsF}_2 \rightarrow \text{CsF} + \frac{1}{2}\text{F}_2(\text{g})$; (b) CsF_3
 63 $\rightarrow \text{CsF} + \text{F}_2(\text{g})$; (c) $\text{CsF}_5 \rightarrow \text{CsF} + 2\text{F}_2(\text{g})$.
 64
 65

66 III. STABILITY OF CsF_n (n>1) COMPOUNDS UNDER PRESSURE

67 The detailed results for variable-composition structure searches between CsF and F, are shown in Fig. S5. There
 68 is clearly a general trend that the formation enthalpies of CsF_n (n≥1) compounds decrease with pressure, suggesting
 69 that the Cs atoms can be oxidized further.

70 For the predicted stable high pressure phases, we calculated phonon frequencies throughout the Brillouin zone using
 71 the finite-displacement approach as implemented in the Phonopy code. As shown in Fig. S6, the absence of imaginary
 72 frequencies ensures that the obtained structures are dynamically stable.
 73

75 IV. CRYSTALLOGRAPHIC DATA

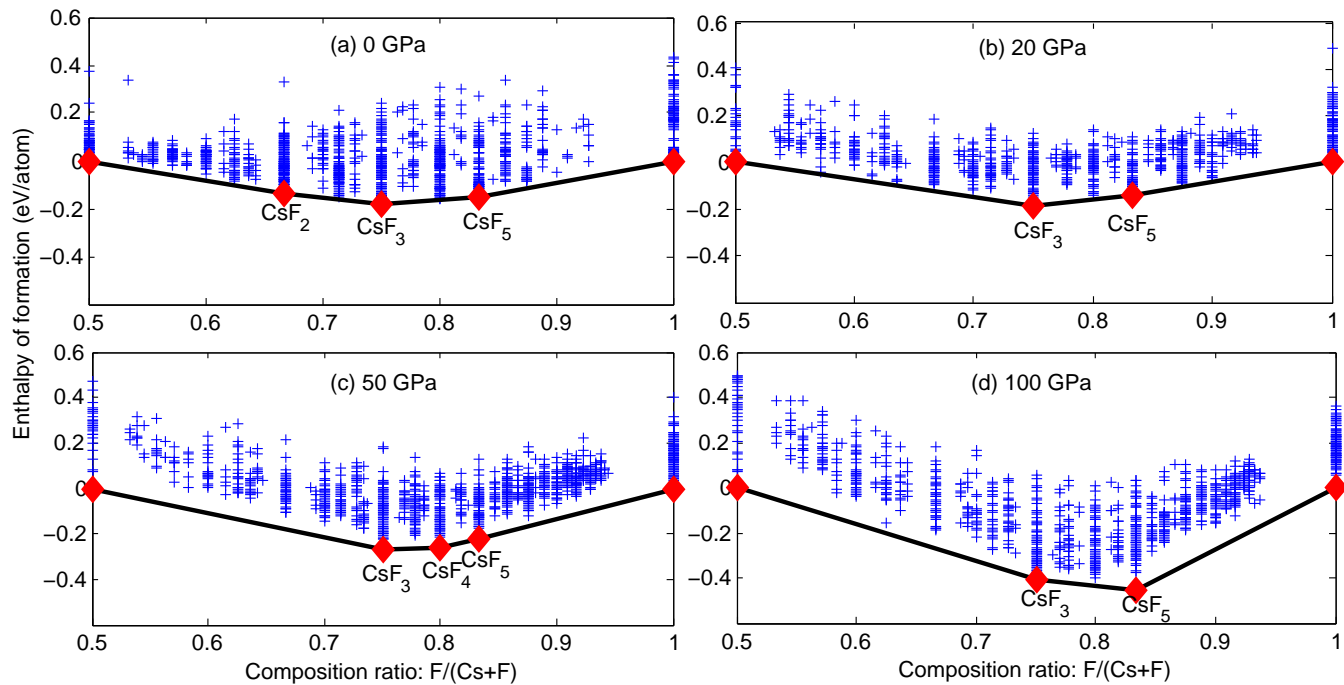


FIG. S5. Relatively stabilities for all compounds in the CsF-F system at (a) 0 GPa; (b) 20 GPa; (c) 50 GPa; and (d) 100 GPa, respectively.

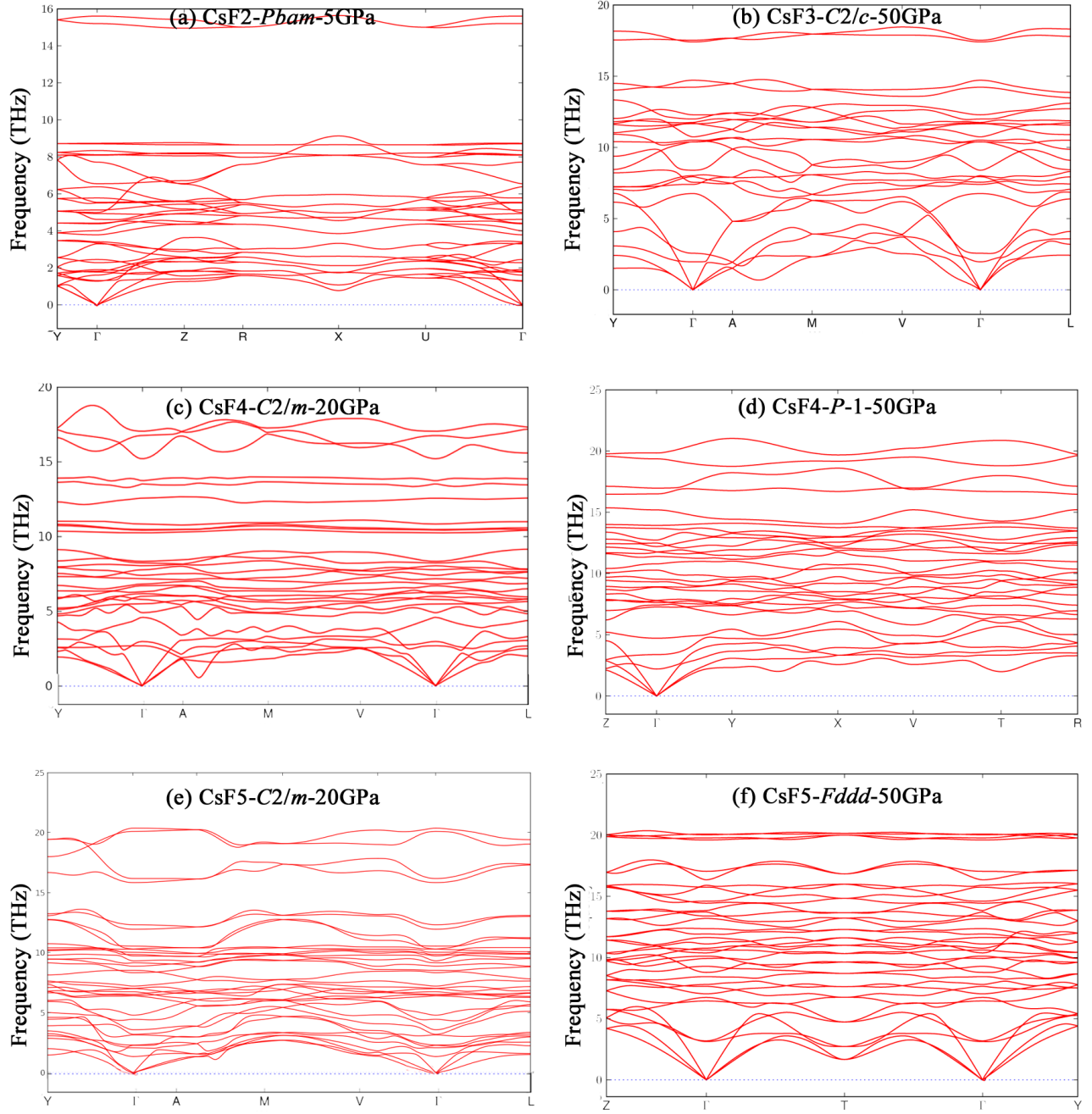


FIG. S6. Phonon dispersion curves of CsF_n compounds (a) *Pbam*-CsF₂ at 5 GPa; (b) *C2/c*-CsF₃ at 50 GPa; (c) *C2/m*-CsF₄ at 20 GPa; (d) *P1*-CsF₄ at 50 GPa; (e) *C2/m*-CsF₅ at 20 GPa; and (f) *Fddd*-CsF₄ at 50 GPa respectively.

TABLE S1. The detailed crystal structures of CsF_n compounds at different pressures.

Phase	Pressure (GPa)	Space group	Lattice parameters	Atomic coordinates
CsF ₂	0	<i>I4/mmm</i>	a= 4.111 Å c=16.163 Å	Cs(4e) 0.000 0.000 0.861 F1(4e) 0.000 0.000 0.682 F2(4e) 0.000 0.000 0.554
CsF ₂	10	<i>Pbam</i>	a= 7.862 Å b= 7.365 Å c= 3.635 Å	Cs(4g) 0.167 0.666 0.000 F1(4h) 0.039 0.107 0.500 F2(4h) 0.372 0.864 0.500
CsF ₃	0	<i>R$\bar{3}m$</i>	a= 5.455 Å c= 9.415 Å	Cs(3a) 0.000 0.000 0.000 F1(3b) 0.000 0.000 0.500 F2(6c) 0.000 0.000 0.315
CsF ₃	100	<i>C2/c</i>	a= 6.322 Å b= 3.692 Å c= 6.382 Å $\beta=100.65^\circ$	Cs(4c) 0.250 0.250 0.000 F1(4e) 0.000 0.163 0.250 F2(8f) 0.612 0.172 0.119
CsF ₄	20	<i>C2/m</i>	a= 7.207 Å b= 4.609 Å c= 8.724 Å $\beta=58.43^\circ$	Cs1(2a) 0.000 0.000 0.000 Cs2(2b) 0.000 0.000 0.500 F1(4i) 0.189 0.000 0.607 F2(4i) 0.417 0.000 0.215 F3(4i) 0.429 0.000 0.611 F4(4i) 0.756 0.000 0.866
CsF ₄	50	<i>P-1</i>	a= 6.064 Å b= 4.101 Å c= 4.031 Å $\alpha=88.68^\circ$ $\beta=84.76^\circ$ $\gamma=92.32^\circ$	Cs1(1a) 0.000 0.000 0.000 Cs2(1b) 0.500 0.500 0.500 F1(2i) 0.527 0.780 0.913 F2(2i) 0.197 0.629 0.979 F3(2i) 0.269 0.980 0.448 F4(2i) 0.916 0.645 0.515
CsF ₄	70	<i>P-1</i>	a= 6.732 Å b= 3.814 Å c= 7.128 Å $\alpha=97.63^\circ$ $\beta=88.30^\circ$ $\gamma=89.31^\circ$	Cs1(2i) 0.858 0.070 0.244 Cs2(2i) 0.604 0.356 0.751 F1(2i) 0.086 0.738 0.496 F2(2i) 0.863 0.153 0.972 F3(2i) 0.964 0.530 0.792 F4(2i) 0.444 0.786 0.585 F5(2i) 0.526 0.215 0.103 F6(2i) 0.737 0.680 0.073 F7(2i) 0.253 0.301 0.609 F8(2i) 0.236 0.081 0.310
CsF ₅	0	<i>P2₁</i>	a= 5.858 Å b= 8.235 Å b= 5.184 Å $\beta=106.67^\circ$	Cs(2a) 0.815 0.000 0.740 F1(2a) 0.777 0.234 0.232 F2(2a) 0.744 0.603 0.505 F3(2a) 0.220 0.267 0.764 F4(2a) 0.286 0.972 0.283 F5(2a) 0.517 0.250 0.014
CsF ₅	10	<i>C2/c</i>	a= 7.794 Å b= 4.440 Å c= 3.613 Å $\beta=79.81^\circ$	Cs(4e) 0.000 0.801 0.250 F1(4e) 0.000 0.342 0.250 F2(8f) 0.327 0.013 0.719 F3(8f) 0.679 0.382 0.708
CsF ₅	30	<i>C2/m</i>	a= 8.338 Å b= 4.314 Å b= 5.292 Å $\beta=42.02^\circ$	Cs(2a) 0.000 0.000 0.000 F1(2c) 0.000 0.000 0.500 F2(4i) 0.345 0.000 0.497 F3(4i) 0.714 0.000 0.926
CsF ₅	100	<i>Fdd2</i>	a=13.726 Å b= 5.357 Å c= 5.146 Å	Cs(8a) 0.000 0.000 0.228 F1(8a) 0.000 0.000 0.853 F2(16b) 0.576 0.146 0.022 F3(16b) 0.162 0.499 0.346