Supporting Information

Pressure-Stabilized Zinc Trifluoride

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1. Computational details

The search for the possible candidate structures was made on diverse stoichiometries of ZnF_x (x = 1/3, 1/2, 2/3, 1, 2, 3, 4, 5, 6, 7 and 8) by simulation cells containing up to four formula units. Structure searches for all stoichiometries were implemented at multiple pressures, e.g., 0, 50, 100, 200, 300, 400 GPa at 0 K, using the particle swarm optimization method carried out by the CALYPSO (Crystal structure AnaLYsis by Particle Swarm Optimization)¹⁻² Program. There are 50 structures in each generation, and the structures in the first generation were generated randomly restraining by symmetry. Then, 60% of the structures in the first generation with lower enthalpies are chosen to produce the structures in the next generation. 40% of the structures in the new generation are generated randomly. All of the predicted structures are optimized to their local minimums by means of VASP code³ and stopped when total energy changes are lower than 1×10^{-5} eV per cell. In order to avoid identical structures, a structure fingerprinting method of bond characterization matrix is employed in the structure generation. These procedures enhance the structure diversity to a great degree, which is essential for the searching efficiency of algorithm. In general, structural searching simulations for each stoichiometry were stopped after 30 generations (1500 structures).

After the structure searching simulations, we choose a quantity of structures with lower enthalpies and perform structural optimization as a function of pressure in the framework of density functional theory by means of the Vienna ab initio simulation package (VASP) Program³ with higher accuracy. The Perdew-Burke-Ernzerh (PBE)⁴ function in the generalized gradient approximation (GGA)⁵ was used. The projector-augmented-wave (PAW)⁶ method was employed with the Zn and F potentials obtained from the VASP potential library. The 3d¹⁰4s² and 2s²2p⁵ electrons are treated as the valence electrons of Zn and F atoms, respectively. The cutoff energy was set as 600 eV. A dense k-point grid⁷ with a spacing of $2\pi \times 0.03$ Å⁻¹ was used to sample the Brillouin Zone, which ensures the total energy converged within 1 meV/atom. The generalized gradient approximation (GGA) function is unable to describe the van der Walls (vdW) interaction correctly, and the layer structures and weak interactions may appear in the predicted phase of Zn-F system, therefore we adopted the vdW-DF⁸⁻¹⁰ by using revPBE, and two "opt" functions (optB88-vdW and optPBE-vdW)¹¹⁻¹² where the exchange functions are optimized for the correlation part to confirm the phase stability of Zn fluorides. As for electronic property calculations, the hybrid functional in the the frame work of Heyd-Scuseria-Ernzerhof (HES06)¹³ is the most effective and frequently used method to verify the calculation results of the traditional DFT. The accuracy of HSE calculation is significantly high, whereas the time using is extraordinarily long. Based on this, we employ an HSE06 calculation to validate the metallicity of ZnF_3 , and verify the contributions of different orbitals in ZnF_3 .

Crystal orbital Hamiltonian population (COHP) was calculated using the LOBSTER code.¹⁴ The phonon frequencies of all the structures were determined using the supercell method with the PHONOPY code.¹⁵



2. Relative enthalpies of formation of Zn-F phases with respect to solid Zn and F

Figure S1. Relative enthalpies of formation of Zn-F phases with respect to solid Zn and F. Stable phases (solid squares) are connected by solid lines in the convex hulls. Unstable/metastable phases are indicated by open squares.



3. Enthalpies of various predicted ZnF₂ as a function of pressures

Figure S2. Enthalpies (relative to $P4_2/mnm$ phase) of various predicted ZnF₂ phases as a function of pressures.



4. Crystal structures of predicted stable ZnF₂

Figure S3. Crystal structures of stable ZnF_2 . (a) $P4_2/mnm$ at 1 atm. (b) Pnnm at 10 GPa. (c) $Pa\overline{3}$ at

20 GPa. (d) *Pnma* at 50 GPa. The large purple and small green balls represent Zn and F atoms, respectively.



5. Electronic band structure and projected DOS of the Pnma ZnF₂

Figure S4. Calculated electronic band structure and projected DOS of the $PnmaZnF_2$ at 50 GPa. (a) Used by normal PBE. (b) Used by hybrid functional HSE06.¹³

6. Electronic DOS of Cccm ZnF₃ used by normal PBE and HSE06



Figure S5. Calculated projected DOS of the *Cccm* ZnF_3 at 200 GPa. (a) Used by normal Perdew-Burke-Ernzerhof. (b) Used by hybrid functional Heyd-Scuseria-Ernzerhof (HSE06).¹³

7. Projected DOS of the d orbital of Cccm ZnF₃ as a function of pressures



Figure S6. Calculated projected DOS of the d orbital of *Cccm* ZnF₃ as a function of pressures.

8. Phase stability of *Cccm* ZnF_3 with and without van der Waals (vdW) interactions



Figure S7. Phase stability of *Cccm* ZnF_3 with respect to ZnF_2 and F_2 using PBE, optB88-vdW¹¹⁻¹², optPBE-vdW¹¹⁻¹² and vdW-DF⁸⁻¹⁰ functions.

9. Thermodynamics of the ZnF₃ dissociation



Figure S8. Calculated ΔH , ΔU and ΔPV as a function of pressures of ZnF₃ with respect to ZnF₂ plus 1/2 F₂. The change of enthalpy (ΔH), internal energy (ΔU) and $\Delta(PV)$ are defined as $\Delta H = H(ZnF_3) - (H(ZnF_2) + 1/2 H(F_2))$, $\Delta U = U(ZnF_3) - (U(ZnF_2) + 1/2 U(F_2))$, $\Delta(PV) = PV(ZnF_3) - (PV(ZnF_2) + 1/2 PV(F_2))$, where *P* and *V* are the pressure and volume per formula unit, respectively.



10. Phonon dispersion curves for predicted stable Zn-F compounds

Figure S9. Phonon dispersion curves of the predicted Zn-F binary compounds. (a) $P4_2/mnm$ ZnF₂ at 1 atm. (b) *Pnnm* ZnF₂ at 10 GPa. (c) $Pa\overline{3}$ ZnF₂ at 20 GPa. (d) *Pnma* ZnF₂ at 50 GPa. (e) *Cccm* ZnF₃ at 200 GPa.

11. Structural information of the predicted stable Zn-F compounds

	Space	Lattice	Atomic coordinates			
	group	Parameters		(fractional)		
		(Å, °)	Atoms	Х	Y	Ζ
ZnF_2	P4 ₂ /mnm	a=b=4.80060	Zn(2b)	0.00000	0.00000	0.50000
(0 GPa)		c=3.18770	F(4g)	0.19559	0.80441	0.00000
		α=β=γ=90.000				
ZnF ₂	Pnnm	a=4.49460	Zn(2b)	0.00000	0.00000	0.50000
(10 GPa)		b=4.73490	F(4g)	-0.23615	0.16029	0.00000
		c=3.11770				
		α=β=γ=90.0000				
ZnF ₂	$Pa\overline{3}$	a=b=c=4.89360	Zn(4a)	0.00000	0.50000	0.50000
(20 GPa)		α=β=γ=90.0000	F(8c)	0.65270	0.84730	0.15270
ZnF ₂	Pnma	a=5.10440	Zn(4c)	0.74600	0.75000	0.11433
(50 GPa)		b=3.10990	F1(4c)	0.85403	0.25000	0.92695
		c=6.04170	F5(4c)	0.97741	0.25000	0.33055
		α=β=γ=90.0000				
ZnF ₃	Ссст	a=5.04820	Zn(4f)	0.75000	0.25000	0.00000
(200 GPa)		b=5.04890	F1(8l)	0.37497	0.12504	0.00000
		c=3.61080	F2(4a)	0.00000	0.00000	0.25000
		α=β=γ=90.0000				

Table S1. Calculated structural parameters of the predicted stable Zn-F compounds.

12. Bader charge analysis of *Pnma* ZnF₂ and *Cccm* ZnF₃.

Table S2. Calculated Bader charge analysis of the *Pnma* ZnF_2 and *Cccm* ZnF_3 . ΔQ is the charge transfer in e per atom. The number in parentheses is the Wyckoff sites corresponding to the atoms.

Phase	Pressure (GPa)	Q (Zn/e)	$\Delta Q (Zn/e)$	Q (F/e)	$\Delta Q (F/e)$
<i>Pnma</i> ZnF ₂	50	10.50 (4c)	-1.50	7.74 (4c)	+0.74 (F1)
				7.76 (4c)	+0.76 (F5)
Cccm ZnF ₃	200	10.41 (4f)	-1.59	7.52 (81)	+0.52 (F1)
				7.55 (4a)	+0.55 (F2)

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