Electronic Supplementary Information* (ESI) for the article

Low-temperature formation of cubic β-PbF_2: precursor-based synthesis and first-principles phase stability study‡

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Counterpoise-corrected calculations for single ions. Only a single ion was considered in these calculations, but the basis sets of its neighbours, placed at their respective optimized positions as in the crystal, were included in the calculation. The numbers of neighbours included are 23 for Pb^{2+}, 18 for $F(1)^-$ and 19 for $F(2)^-$ for the orthorhombic α-phase, and 20 for Pb^{2+} and 22 for F^- for the cubic β-phase.

Equilibrium geometric structure of crystal unit cells. Closer inspection of the data in Table S1 shows that the functionals B3PW and PW91 perform best for the orthorhombic α-polymorph, whereas the functionals PW91 and PBE give the best results for the cubic β-polymorph. The functional SVWN yields crystal structures that are too compact. Only with this latter functional the α-phase is found at lower energy than the β-phase, so that the unphysical result of a *negative* transition pressure follows.

Elastic constants. The energies calculated for distorted structures were fitted to a fourth-order polynomial, $E(\delta) - E(0) = a_2\delta^2 + a_3\delta^3 + a_4\delta^4$. The quantity $2a_2/V$ represents, in general, a linear combination of some elastic constants $C_{ij} = \left(V^{-1}\partial^2 E/\partial\varepsilon_i\partial\varepsilon_j\right)_0$. Hence, the complete set of elastic constants can be determined finally by solving a set of linear equations. In general, the bulk modulus is related to the elastic constants through $B = {}^{1}\!/_{9}(C_{11} + C_{22} + C_{33} + 2C_{12} + 2C_{13} + 2C_{23})$. For cubic cases, this reduces to $B = {}^{1}\!/_{3}(C_{11} + 2C_{12})$, due to symmetry. The agreement between theory and experiment is well acceptable for the cubic β-polymorph, for which experimental data for the full set of elastic constants is available,[7] Since the experiments have been performed at ambient temperature, the calculated values are expected to be higher than the experimental ones. In fact, this is always the case.

Equation of state. For each polymorph, the Murnaghan equation of state[37,38] was used to convert the calculated data points $E(V_i)$ into a closed-form expression. The calculated data points were fitted to

$$E(V) - E(V_0) = B_0 V_0 f(V/V_0)\,, \quad \text{where} \quad f(x) = \frac{1}{B'_0}\left\{x - 1 + \frac{1}{B'_0 - 1}\left(\left(\frac{1}{x}\right)^{B'_0 - 1} - 1\right)\right\}$$

and $B_0 = B(P = 0)$, $B'_0 = \partial B/\partial P|_0$. The bulk modulus at vanishing pressure, B_0, and its pressure derivative, B'_0, were considered as free parameters, whereas the equilibrium volume, V_0, and the total energy corresponding to it, $E(V_0)$, where taken without change from the previous crystal structure optimization step.

Zero-point vibrational energy. The Debye theory for the solid[47] gives $E_{\mathrm{ZPV}} = {}^{9}\!/_{8}\, pR\Theta_{\mathrm{D}}$, with p number of atoms per cell ($p = 3$ for a formula unit, i. e., $Z = 1$), R molar gas constant, Θ_{D} Debye temperature (188 K for α-PbF_2, 237 K for β-PbF_2).[48] Hence, the zero-point vibrational energy difference per mole of formula units is $\Delta E_{\mathrm{ZPV}} = E_{\mathrm{ZPV},\alpha} - E_{\mathrm{ZPV},\beta} = {}^{27}\!/_{8} R\Delta\Theta_{\mathrm{D}} = -1.375$ kJ/mol.

Conversion relations. The following short list provides some conversion relations that proved useful for the work presented here (data taken mainly from refs. 28 and 34).
The atomic unit of energy: $E_{\mathrm{h}} = 1$ hartree $= 4.35974394$ aJ $= 27.21138386$ eV.
The pressure: $1\ E_{\mathrm{h}}/\text{Å}^3 = 4359.74812$ GPa.
The elementary charge: $e = 1.602176487 \times 10^{-19}$ C.
The dipole moment: 1 D (Debye) = 3.33564×10^{-30} C m.

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‡ Reference numbers refer to the list of references in the main article

Table S1 Parameters characterising the equilibrium structure and the charge density distribution of the two crystalline polymorphs of lead(II) fluoride, PbF$_2$, and of the isolated monomer (partial charges from Mulliken population analysis, see Table S2 for associated energetic data and see the text for computational details)

	This work					Other	Expt.[b]
	SVWN	PBE	PW91	B3LYP	B3PW	calcs.[a]	
			α-PbF$_2$ (orthorhombic cotunnite-type structure, primitive cell, $Z = 4$)				
a / pm	621.4	648.4	646.6	652.5	645.6	656.2	644.0
b / pm	378.2	392.8	391.7	394.0	390.7	393.2	389.9
c / pm	744.2	770.4	768.5	774.5	769.0	762.0	765.1
x(Pb)	0.2527	0.2550	0.2548	0.2550	0.2550	0.245	0.2527
z(Pb)	0.1128	0.1018	0.1025	0.0988	0.1007	0.114	0.1042
x(F(1))	0.8596	0.8589	0.8589	0.8592	0.8592	0.856	0.8623
z(F(1))	0.0629	0.0700	0.0696	0.0692	0.0676	0.072	0.0631
x(F(2))	0.4684	0.4809	0.4803	0.4812	0.4796	0.473	0.4662
z(F(2))	0.8398	0.8498	0.8494	0.8529	0.8523	0.826	0.8457
$V_{0,\alpha}$ / 10^{-3} nm^3	174.92	196.22	194.63	199.07	193.97	196.61	192.11
ρ_α / g cm^{-3}	9.34	8.33	8.39	8.21	8.42	8.31	8.47
q(Pb) / e [c]	1.527	1.539	1.541	1.614	1.603	—	—
q(F(1)) / e	−0.755	−0.765	−0.766	−0.802	−0.798	—	—
q(F(2)) / e	−0.772	−0.774	−0.775	−0.812	−0.805	—	—
			β-PbF$_2$ (cubic fluorite-type structure, conventional cell, $Z = 4$)				
a / pm	578.0	595.4	594.2	596.8	592.8	598.5	594.6
$V_{0,\beta}$ / 10^{-3} nm^3	193.06	211.11	209.80	212.61	208.28	214.38	210.25
ρ_β / g cm^{-3}	8.46	7.74	7.79	7.68	7.84	7.62	7.74
q(Pb) / e	1.533	1.556	1.558	1.629	1.624	—	—
q(F) / e	−0.767	−0.778	−0.779	−0.815	−0.812	—	—
			PbF$_2$ molecule ($\tilde{X}\ {}^1A_1$)				
r(Pb-F) / pm	203.5	207.3	207.0	206.2	205.0	204.7	204.1
ϕ(F-Pb-F) / °	96.31	97.73	97.57	97.27	96.97	96.7	97
μ / D [d]	4.664	4.877	4.887	5.146	5.029	5.52	—
q(Pb) / e [e]	1.039	1.070	1.068	1.153	1.147	—	—
q(F) / e [e]	−0.520	−0.535	−0.534	−0.577	−0.573	—	—

[a] From refs. 17 for the solids (*ab initio* perturbed ion method, combined with the LYP[27] density functional to estimate correlation energy) and 49 for the monomer (r_e structure from relativistic MP2 calculations)

[b] From refs. 1 (neutron diffraction study of polycrystalline α-PbF$_2$), 2 (neutron diffraction study at 295 K of polycrystalline β-PbF$_2$) and 50 (r_g structure from gas-phase electron diffraction for PbF$_2$)

[c] $e = 1.602176487 \times 10^{-19}$ C

[d] 1 D (Debye) = 3.33564×10^{-30} C m

[e] The partial charges for the monomer are *not* consistent with the observable dipole moment

Table S2 Energetic data for the two crystalline polymorphs of lead(II) fluoride, PbF_2, and for the isolated monomer. Total energies (in $E_h{}^a$) per formula unit of the crystal, for the isolated ions (counterpoise corrected) and for the isolated monomer (see Table S1 for associated optimized structural parameters); resulting lattice and binding energies, and their differences (in different units)

	SVWN	PBE	PW91	B3LYP	B3PW
PbF_2 molecule ($\widetilde{X}\ {}^1A_1$, optimized molecular structure)					
E_{tot}(free monomer) / E_h	−391.145845	−392.512844	−392.724428	−392.580776	−392.697274
α-PbF_2 (orthorhombic cotunnite-type structure, fully optimized)					
E_{tot}(formula unit) / E_h	−391.235751	−392.569084	−392.781388	−392.634642	−392.745511
$E_{tot}(Pb^{2+})$ / E_h	−191.785370	−192.094220	−192.167519	−192.054050	−192.175415
$E_{tot}(F(1)^-)$ / E_h	−99.221861	−99.767936	−99.836161	−99.826226	−99.821943
$E_{tot}(F(2)^-)$ / E_h	−99.221746	−99.767705	−99.835993	−99.825958	−99.821728
$E_{lat} = E_{tot}(\text{formula unit}) - \left(E_{tot}(Pb^{2+}) + E_{tot}(F(1)^-) + E_{tot}(F(2)^-)\right)$					
in E_h	−1.006774	−0.939223	−0.941714	−0.928408	−0.926426
in eV	−27.395722	−25.557567	−25.625351	−25.263273	−25.209335
$E_b = E_{tot}(\text{formula unit}) - E_{tot}(\text{free monomer})$					
in E_h	−0.087608	−0.056944	−0.057785	−0.055043	−0.049406
in eV	−2.383942	−1.549531	−1.572418	−1.497791	−1.344399
β-PbF_2 (cubic fluorite-type structure, fully optimized)					
E_{tot}(formula unit) / E_h	−391.233453	−392.569788	−392.782214	−392.635819	−392.746679
$E_{tot}(Pb^{2+})$ / E_h	−191.784622	−192.093548	−192.166824	−192.053389	−192.174770
$E_{tot}(F^-)$ / E_h	−99.218494	−99.764488	−99.832598	−99.823383	−99.819348
$E_{lat} = E_{tot}(\text{formula unit}) - \left(E_{tot}(Pb^{2+}) + 2E_{tot}(F^-)\right)$					
in E_h	−1.011843	−0.947265	−0.950195	−0.935663	−0.933212
in eV	−27.533643	−25.776386	−25.856114	−25.460698	−25.394003
$E_b = E_{tot}(\text{formula unit}) - E_{tot}(\text{free monomer})$					
in E_h	−0.089907	−0.056240	−0.056959	−0.053866	−0.048238
in eV	−2.446487	−1.530366	−1.549937	−1.465772	−1.312615
Resulting energy differences (always taken as $\Delta E = E_\alpha - E_\beta$)					
$\Delta E_b = \Delta E_0$					
in meV	−62.55	19.17	22.48	32.02	31.78
in kJ/mol	−6.035	1.849	2.169	3.089	3.067
in kcal/mol	−1.441	0.442	0.518	0.738	0.732
ΔE_{lat}					
in meV	137.9	218.8	230.8	197.4	184.7
in kJ/mol	13.31	21.11	22.27	19.05	17.82
in kcal/mol	3.178	5.043	5.318	4.550	4.256

[a] E_h = 1 hartree = 4.35974394 aJ = 27.21138386 eV is the atomic unit of energy (from ref. 34)

Table S3 Elastic constants (in GPa) for the two polymorphs of lead(II) fluoride, PbF_2

	This work					Other	Expt.[b]
	SVWN	PBE	PW91	B3LYP	B3PW	calcs.[a]	
	α-PbF_2 (orthorhombic cotunnite-type structure, primitive cell)						
B	80.0	50.0	53.2	50.4	48.9	63.2	47.0 (56)[e]
C_{11}	107	82.9	92.5	89.6	88.8	87	—
C_{22}	119	87.3	96.2	97.0	95.8	103	—
C_{33}	130	78.3	87.6	78.5	77.5	93	—
C_{12}[c]	60.5	33.0	37.4	34.9	34.9	47	—
C_{13}[c]	56.5	29.4	33.6	29.5	28.5	46	—
C_{23}[c]	64.5	34.8	39.3	35.7	33.9	50	—
C_{44}	6.74	6.06	7.71	8.16	7.46	20	—
C_{55}	24.4	14.6	16.9	16.2	16.3	23	—
C_{66}	36.9	29.1	31.4	31.4	32.4	27	—
	β-PbF_2 (cubic fluorite-type structure, primitive cell)						
B	95.9	74.5	76.3	76.0	76.8	69.7	63.4 (69.5)[e]
C_{11}[d]	135	115	118	121	120	105	96.1
C_{12}[d]	76.1	53.9	55.4	53.7	55.0	52	47.1
C_{44}	27.6	24.2	25.0	26.3	26.1	27.8	20.8

[a] Ref. 15

[b] Refs. 44 (ambient temperature) and 15 (extrapolation to 0 K) for α-PbF_2, and ref. 7 for β-PbF_2

[c] From the relations $C_{sa} = 1/4(C_{11} + C_{22} - 2C_{12})$, $C_{sb} = 1/4(C_{11} + C_{33} - 2C_{13})$ and $C_{sc} = 1/4(C_{22} + C_{33} - 2C_{23})$

[d] From the relations for the bulk modulus $B = 1/3(C_{11} + 2C_{12})$ and the shear modulus $C_s = 1/2(C_{11} - C_{12})$

[e] Value in parentheses from extrapolation to 0 K