Table S1. X-ray powder diffraction data for $Ba(SbF_6)_2 \cdot 5XeF_2$

d_{calc}/pm	I[a]	d_{obs}/pm	I[b]
680.0	11.7		
451.7	12.0		
379.0	1000.0	376.6	vs
379.0	999.9		
348.3	372.1	351.0	s
340.0	270.3	341.1	s
302.2	282.0	302.8	s
297.0	9.5		
297.0	9.2		
276.1	8.1		
252.7	14.1		
252.6	14.1		
243.3	116.7	244.6	s
243.3	116.5		
232.2	11.2		
228.2	228.3	227.9	s, br
225.9	181.5		
206.5	157.9	207,8	s
206.5	158.0		
203.0	157.9	203.2	s
203.0	158.0		
189.5	130.1	190.0	s
189.5	130.5		
186.1	114.3	186.1	s
186.1	114.1		
174.1	48.3	175.7	vw

170.0	50.0	170.8	vw
156.7	69.8	157.1	m, br
156.6	69.5		
155.0	25.1		
155.0	25.2		
152.8	32.3	153.6	vw
152.8	32.0		
151.1	26.7	151.7	vw
150.9	63.7		
148.5	51.0	147.9	m, br
148.5	50.8		
148.2	40.0		
147.2	50.0		
147.2	50.3		
138.6	31.1	139.1	m, br
138.1	45.9		
137.9	37.6		
137.9	37.7		
136.3	38.8	136.5	m
136.3	38.7		
133.1	30.2	133.8	vw
133.1	29.9		
130.3	27.4	130.7	vw
130.3	27.4		
128.3	26.6	128.3	vw
128.3	26.5		
126.3	22.6	126.3	vw
126.3	22.6		
121.7	9.7	122.3	vw

121.6	9.7		
117.3	16.6	117.0	w
117.3	16.5		
116.5	17.0		
116.5	17.1		
116.1	9.6		
115.2	14.0		
115.2	14.0		
114.1	14.5		
113.3	7.7	113.3	w
113.0	13.9		
113.0	13.9		
112.9	13.5		
112.9	14.0		
112.8	14.0		
111.3	12.8		
111.3	12.8		
108.4	9.8	108.6	vw
108.2	10.6		
108.2	10.6		
107.4	10.1		
107.4	10.2		
106.1	9.4	105.6	vw
105.9	10.1		
105.9	10.1		
105.4	9.7		
105.4	9.7		
103.3	7.9		
103.2	7.9		

102.3	8.0		
102.3	8.1		
101.5	7.9	101.5	vw
101.5	7.9		
101.4	8.0		
101.4	8.0		

[a] Calculated *d* values from the crystal structure, only the peaks, stroger than 0.70 % are shown.
[b] very strong: vs, strong: s, medium: m, weak: w, very weak: vw, broad line: br.

Table S2: Atomic coordinates and equivalent displacement parameters U_{eq} in $Ba(SbF_6)_2 \cdot 5XeF_2$

Atom	x/a	y/b	z/c	$U_{eq}(Å^2)$[a]
Ba1	0	0	0	0.0208(3)
Xe1	1/2	0	0	0.0463(4)
Xe2	1/4	1/4	0	0.0242(3)
Xe3	0	0	1/2	0.0408(4)
Xe4	1/2	0	1/2	0.0405(4)
Sb1	1/4	1/4	1/2	0.0216(3)
F1	0.3545(13)	0	0.002(2)	0.0980(40)
F2	0.1161(5)	0.1842(5)	-0.0001(7)	0.0504(17)
F3	-0.0585(10)	0	0.2448(15)	0.0750(30)
F4	0.3037(10)	0	0.2436(15)	0.0740(30)
F11	0.1709(5)	0.1233(4)	0.3414(7)	0.0427(14)
F12	0.2720(11)	0.3133(7)	0.3528(12)	0.1140(40)
F13	0.0806(7)	0.3125(7)	0.3534(12)	0.1080(40)

[a] One third of the trace of the orthogonalized U_{ij} tenzor.