Supplementary Information

X-ray and neutron diffraction studies of single-crystal cubic $Cs_2(HSO_4)(H_2PO_4)$

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Table S1. Experimental details and refinement statistics of diffraction measurements for $Cs_2(HSO_4)(H_2PO_4)$* in space group $Pm\bar{3}m$.

Measurement	298 K, XRD crystal 1	200 K, XRD crystal 2§	100 K, XRD crystal 3§	100 K, ND crystal 4
Radiation	Mo Ka (λ = 0.71073 Å)	Mo Ka (λ = 0.71073 Å)	Mo Ka (λ = 0.71073 Å)	Neutron ToF
Temperature	298 K	200 K	100 K	100 K
Lattice parameter, Å	4.9004(4)	4.8552(9)	4.8664(5)	4.886(3)
Unit cell volume, $Å^3$	117.68(3)	114.45(6)	115.25(2)	116.64(3)
Z	1	1	1	1
Calculated density, g cm^{-3}	3.223	3.314	3.291	3.295
Absorption coefficient, mm^{-1}	8.300	8.377	8.314	0.05045
F(000)	102	102.5	102.5	105.5
2Θ range (°)	4.1330 – 28.0080	4.2110 – 25.6210	4.1580 – 29.6878	8.439 – 63.094
Index range	-8≤h≤8, -8≤k≤8, -8≤l≤8	-4≤h≤5, -6≤k≤6, -6≤l≤6	-6≤h≤6, -6≤k≤6, -6≤l≤6	-3≤h≤3, -3≤k≤3, -3≤l≤2
Reflections collected	3020	6694**	30477§	98
Independent reflections	92	86	54	9
Data/restraints/parameters	92/0/9	86/0/9	54/0/9	9/0/6
Extinction coefficient	N/A	N/A	N/A	N/A
Largest diff. peak/hole/e A^{-3}	0.117/-0.190	0.24/-0.93	0.19/-0.23	0.033/-0.044 fm A^{-3}
Rint	0.0567	0.0750	0.0622	0.1892
wR2	0.0670	0.0416	0.0339	0.0362
R1	0.0189	0.0156	0.0199	0.0179
GooF	1.020	1.150	1.268	0.785

*The compositions of the individual crystals used in these measurements deviate slightly from the ideal stoichiometry.

** Several datasets from the isothermal hold are combined.

§ The complete data collection during the isothermal hold is combined.

Table S2. Summary of X-ray refinement results of crystals 1-3 examined at several temperatures. Cs resides in the 1*a* site (0,0,0) with an assigned occupancy of 1, S/P in the 1*b* site (½ ½ ½) with assigned occupancies of 0.5/0.5, and O in a 24*l* site (½ *x y*) with an assigned occupancy of 1/6.

Parameter	Crystal 1	Crystal 2		Crystal 3		
Temperature (K)	298*	298	200*	298	200	100*
a (Å)	4.9004(4)	4.8792(6)	4.8552(9)	4.9137(4)	4.8860(5)	4.8664(5)
Cs(U_{11}) (Å^2)	0.1584(8)	0.154(2)	0.169(1)	0.176(1)	0.202(2)	0.198(1)
S/P (U_{11}) (Å^2)	0.123(1)	0.118(3)	0.126(1)	0.134(2)	0.150(2)	0.147(2)
O(*y*)	0.220(2)	0.222(5)	0.219(2)	0.221(4)	0.219(4)	0.220(2)
O(*z*)	0.373(3)	0.368(5)	0.375(3)	0.369(5)	0.375(5)	0.369(3)
O(U_{11}) (Å^2)	0.215(15)	0.16(2)	0.24(2)	0.28(3)	0.27(3)	0.24(1)
O(U_{33}) (Å^2)	0.128(8)	0.11(1)	0.13(1)	0.14(1)	0.14(1)	0.151(8)
O(U_{22}) (Å^2)	0.129(8)	0.10(1)	0.122(7)	0.15(1)	0.15(1)	0.14(1)
O(U_{23}) (Å^2)	-0.009(7)	0.01(1)	0.017(8)	0.005(10)	0.001(10)	0.010(9)
O(U_{eq}) (Å^2)	0.157(7)	0.12(1)	0.166(9)	0.166(9)	0.18(1)	0.181(9)

*stability evaluation condition

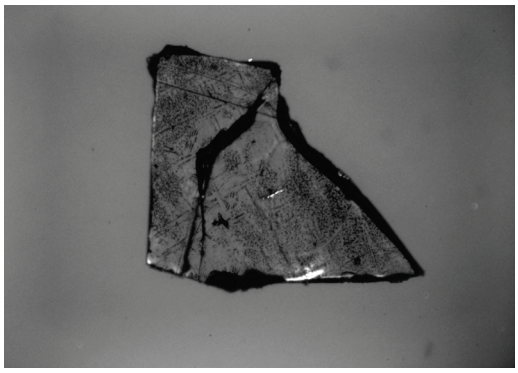
Table S3. References for room temperature crystal structures of compounds in the CsH_2PO_4-$CsHSO_4$ system (Figure S4).

#	Compound	Source	ICSD code
1	$CsHSO_4$-III	Matsunaga 1990[1]	200895
2	$CsHSO_4$-II	Chisholm 2000[2]	91808
3	β-$Cs_3(HSO_4)_{2.5}(H_2PO_4)_{0.5}$	Haile 1998[3]	51116
4	$Cs_4(HSO_4)_3(H_2PO_4)$	Makarova 2016[4]	244159
5	α-$Cs_3(HSO_4)_2(H_2PO_4)$	Haile 1995[5]	79789
6	"$Cs_3(HSO_4)_2(H_2PO_4)$"*	Makarova 2016[4]	244158
7	$Cs_5(HSO_4)_3(H_2PO_4)_2$	Haile 1998[6]	51100
8	$Cs_2(HSO_4)(H_2PO_4)$	Chisholm 1999[7, 8]	280146
9	CsH_2PO_4	Matsunaga 1980[1]	200895

*compound is isostructural to β-$Cs_3(HSO_4)_{2.5}(H_2PO_4)_{0.5}$, raising questions about the compositional analysis

Table S3. Refinement results as a function of hydrogen position on the 6*f* site at (*x* ½ ½). As *x* approaches 1 and the hydrogen approaches the 3*c* site, the refinement statistics monotonically improve.

H position, x	**wR2, R1**	**GooF**	**Oy**	**Oz**	**O-H**	**Uiso**
0.92	0.0908 0.0416	1.969	0.772(4)	0.639(2)	0.99(1)	Cs: 0.16(1) S/P: 0.13(1) O: 0.09(1) H: 0.11(1)
0.93	0.0768 0.0351	1.666	0.773(3)	0.640(2)	1.02(1)	Cs: 0.16(9) S/P: 0.13(1) O: 0.098(9) H: 0.11(1)
0.94	0.0654 0.0310	1.418	0.773(3)	0.641(2)	1.06(1)	Cs: 0.16(8) S/P: 0.133(9) O: 0.104(8) H: 0.125(9)
0.95	0.0564 0.0282	1.225	0.773(2)	0.642(2)	1.10(1)	Cs: 0.162(7) S/P: 0.134(8) O: 0.110(6) H: 0.132(8)
0.96	0.0498 0.0260	1.082	0.774(2)	0.642(1)	1.14(1)	Cs: 0.162(6) S/P: 0.135(7) O: 0.114(5) H: 0.137(7)
0.97	0.0453 0.0244	0.983	0.774(2)	0.643(1)	1.18(1)	Cs: 0.162(5) S/P: 0.136(6) O: 0.117(5) H: 0.141(6)
0.98	0.0424 0.0232	0.921	0.774(2)	0.643(1)	1.223(9)	Cs: 0.162(5) S/P: 0.137(6) O: 0.120(5) H: 0.144(6)
0.99	0.0409 0.0225	0.888	0.774(1)	0.643(1)	1.264(9)	Cs: 0.162(5) S/P: 0.137(6) O: 0.121(4) H: 0.146(5)

(a) 

(b) Xtal transformation.mp4

Figure S1. (a) Single crystal under half polarized light before measurement. b. Video compilation of polarized optical microscopy images.

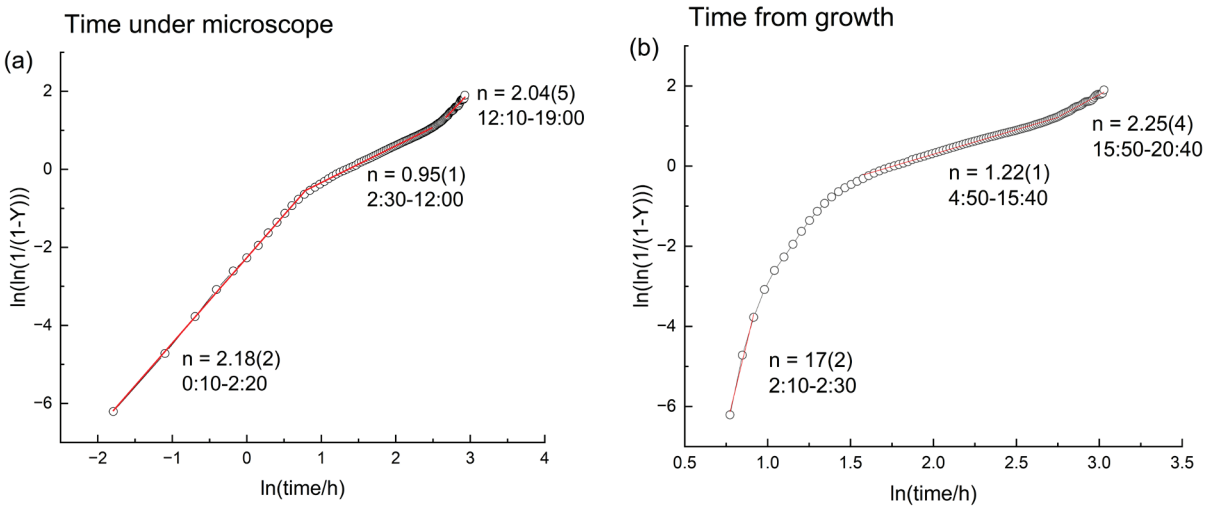


Figure S2. Avrami analysis of the room temperature transformation of a large $Cs_2(HSO_4)(H_2PO_4)$ crystal from the cubic to monoclinic phase: (a) with t = 0 set to the point of collection of the first microscope image, and (b) with t = 0 set to the point of synthesis. Y is the conversion. At longer times than shown (corresponding to > 99.8% conversion), the data appear as scatter plots. In (b), short time data are not available as the first image was captured ~ 2 h from growth.

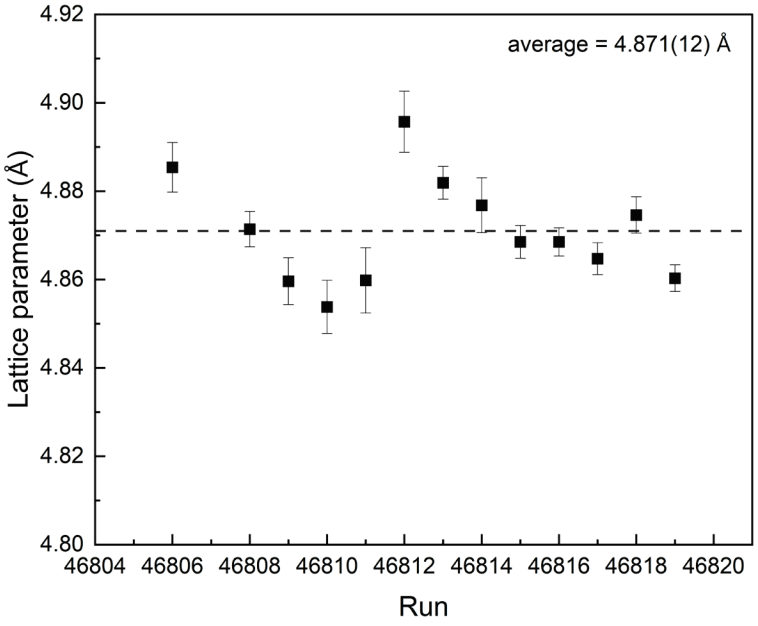


Figure S3. Lattice parameter of cubic single crystal from neutron diffraction measurement, showing minimal evolution over the multiple runs used to obtain sufficient intensity for analysis.

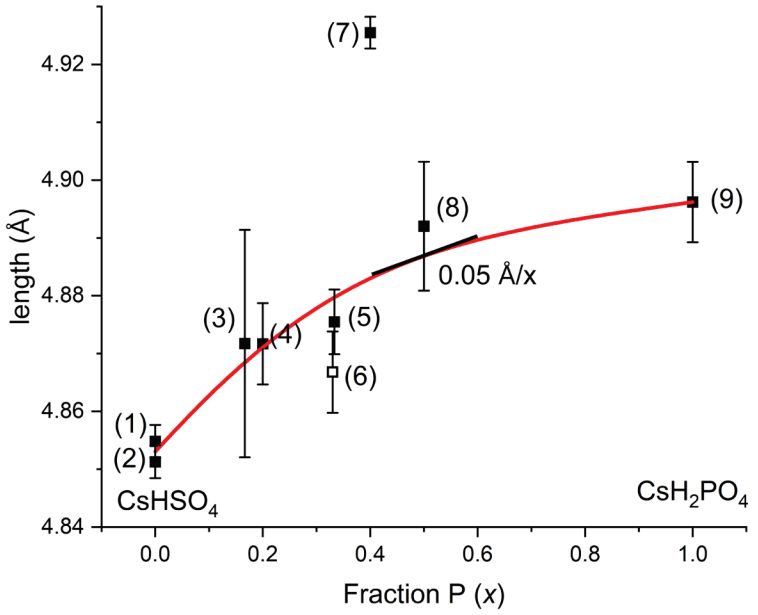


Figure S4. Cell volume trends for (1-*x*)$CsHSO_4$-*x*CsH_2PO_4 compounds. Length is the cube root of the molar volume per CsH_yAO_4 group. Solid line is a guide to the eye ignoring outlier datapoints (6) and (7); it provides an estimate for the composition impact on cell parameter when *x* is close to 0.5.

References

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