Supplementary Materials

Type of the Paper (Article)

Crystal Structure and Theoretical Analysis of $Cs_2Ca_3(SO_4)_4$

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Calculation Setting

The kinetic energy absorption, empty bands, k-point sampling, and pseudopotential used for calculating the birefringence were 310 eV, 12, 1 × 1 × 1, and ultrasoft for $Cs_2Ca_3(SO_4)_4$, 310 eV, 2 × 2 × 1, and ultrasoft for $Cs_2Mg_3(SO_4)_4$, 310 eV, 12, 1 × 1 × 1, and ultrasoft for $Rb_2Mg_3(SO_4)_4$, respectively.

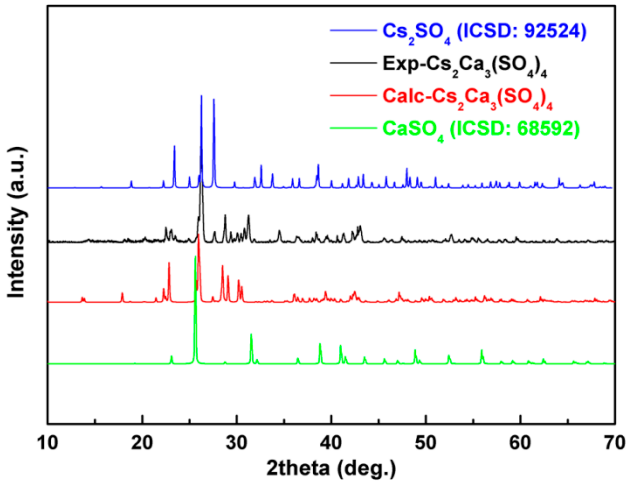

Figure S1. The comparison of XRD patterns with raw reagents of Cs_2SO_4 and $CaSO_4$. Cs_2SO_4-(ICSD: 92524) represents the calculated XRD pattern of Cs_2SO_4 with the Inorganic Crystal Structure Database (ICSD) number of 92524. $CaSO_4$-(ICSD: 68592) represents the calculated XRD pattern of Cs_2SO_4 with the ICSD number of 68592.

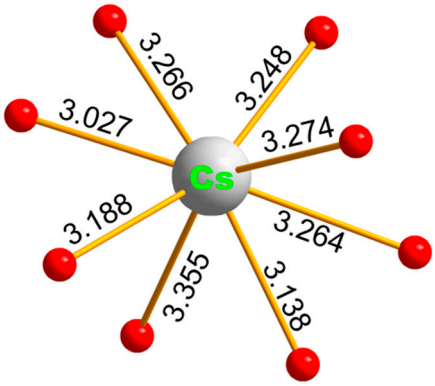

Figure S2. The ball-and-stick representation of a CsO_8 polyhedron in $Cs_2Ca_3(SO_4)_4$.

Table S1. Crystal data and structure refinement for $Cs_2Ca_3(SO_4)_4$.

Formula sum	$Cs_2Ca_3(SO_4)_4$
Formula weight	770.30
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
a (Å)	9.9153(8)
b (Å)	9.3760(6)
c (Å)	9.8044(9)
β	118.365(3)
V (Å^3)	802.04(11)
Z	2
D_{calcd} (g cm^{-3})	3.190
Temperature (K)	299(2)
λ (Å)	0.71073
F (000)	724
Crystal size	0.08 × 0.06 × 0.06 mm^3
Data/restraints/parameters	1635/0/115
μ (mm^{-1})	6.104
GOF (F^2)	1.246
R (int)	0.0506
R_1/wR_2 ($I>2\sigma(I)$)[a]	0.0438/0.0832
R_1/wR_2 (all data)	0.0521/0.0864

[a] $R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$ and $wR_2 = [\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0^2)^2]]^{1/2}$ for $F_o^2 > 2\sigma(F_c^2)$

Table S2. Atom coordinates and equivalent isotropic displacement parameters for $Cs_2Ca_3(SO_4)_4$.

Atom	Wyck.	Symmetry	*x/a*	*y/b*	*z/c*	U_{eq}(Å^2)[a]
Cs1	4e	1	0.66389(5)	0.82800(5)	0.55989(5)	0.0297(2)
Ca1	4e	1	0.24601(14)	0.62804(12)	0.24129(15)	0.0123(3)
Ca2	2a	−1	0	0	0	0.0166(4)
S1	4e	1	0.39243(16)	0.93806(15)	0.14757(18)	0.0107(3)
S2	4e	1	−0.02522(16)	0.34085(15)	0.16829(17)	0.0102(3)
O1	4e	1	0.5390(5)	1.0101(5)	0.2385(6)	0.0259(11)
O2	4e	1	0.3795(5)	0.8283(5)	0.2465(5)	0.0235(11)
O3	4e	1	0.2670(5)	1.0420(5)	0.1031(6)	0.0223(11)
O4	4e	1	0.3848(6)	0.8735(5)	0.0089(6)	0.0274(11)
O5	4e	1	0.1202(6)	0.4159(6)	0.2309(6)	0.0351(14)
O6	4e	1	−0.0740(6)	0.3377(6)	0.2892(6)	0.0331(13)
O7	4e	1	−0.0043(7)	0.1920(5)	0.1399(7)	0.0472(17)
O8	4e	1	−0.1423(6)	0.4069(5)	0.0277(5)	0.0263(12)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S3. Selected bond distances and angles for $Cs_2Ca_3(SO_4)_4$.

Bonds	Bond distances (Å)	Bonds	Bond angles (˚)	Bonds	Bond angles (˚)
Cs(1)-O(2)	3.026(5)	O(1)#5-Ca(1)-O(8)#7	85.63(17)	O(7)-Ca(2)-O(6)#10	86.1(2)
Cs(1)-O(1)	3.266(5)	O(1)#5-Ca(1)-O(6)#1	157.01(19)	O(7)#6-Ca(2)-O(3)#8	93.0(2)
Cs(1)-O(3)#4	3.275(5)	O(2)-Ca(1)-O(6)#11	73.39(18)	O(7)-Ca(2)-O(3)#8	87.0(2)
Cs(1)-O(3)#5	3.354(5)	O(2)-Ca(1)-O(4)#2	87.34(17)	O(7)#6-Ca(2)-O(6)#9	86.1(2)
Cs(1)-O(4)#2	3.188(5)	O(2)-Ca(1)-O(1)#5	83.74(18)	O(7)-Ca(2)-O(6)#9	93.9(2)
Cs(1)-O(5)#1	3.138(5)	O(2)-Ca(1)-O(5)	176.3(2)	O(7)#6-Ca(2)-O(7)	180.0
Cs(1)-O(7)#1	3.263(6)	O(2)-Ca(1)-O(8)#7	94.56(17)	O(7)#6-Ca(2)-O(3)#7	87.0(2)
Cs(1)-O(8)#3	3.248(5)	O(4)#2-Ca(1)-O(5)	93.56(19)	O(7)-Ca(2)-O(3)#7	93.0(2)
Ca(1)-O(1)#5	2.325(4)	O(4)#2-Ca(1)-O(8)#7	167.92(18)	O(6)#9-Ca(2)-O(6)#10	180.0(2)
Ca(1)-O(2)	2.284(5)	O(4)#2-Ca(1)-O(1)#5	82.71(18)	O(1)-S(1)-O(2)	107.2(3)
Ca(1)-O(4)#2	2.312(5)	O(4)#2-Ca(1)-O(6)#1	98.25(18)	O(1)-S(1)-O(3)	109.3(3)
Ca(1)-O(5)	2.324(5)	O(5)-Ca(1)-O(1)#5	92.8(2)	O(2)-S(1)-O(3)	109.5(3)
Ca(1)-O(6)#11	2.526(5)	O(5)-Ca(1)-O(8)#7	83.82(19)	O(4)-S(1)-O(1)	110.9(3)
Ca(1)-O(8)#7	2.354(5)	O(5)-Ca(1)-O(6)#11	110.04(19)	O(4)-S(1)-O(2)	110.2(3)
Ca(2)-O(3)#7	2.376(5)	O(8)#7-Ca(1)-O(6)#1	93.72(17)	O(4)-S(1)-O(3)	109.6(3)
Ca(2)-O(3)#8	2.376(5)	O(3)#7-Ca(2)-O(6)#1	85.15(17)	O(5)-S(2)-O(6)	107.9(3)
Ca(2)-O(6)#9	2.384(5)	O(3)#8-Ca(2)-O(6)#1	94.85(17)	O(5)-S(2)-O(7)	110.0(4)
Ca(2)-O(6)#10	2.384(5)	O(3)#7-Ca(2)-O(6)#9	94.85(17)	O(7)-S(2)-O(6)	105.4(4)
Ca(2)-O(7)#6	2.276(5)	O(3)#8-Ca(2)-O(6)#9	85.15(17)	O(8)-S(2)-O(5)	112.3(3)
Ca(2)-O(7)	2.276(5)	O(3)#7-Ca(2)-O(3)#8	180.0	O(8)-S(2)-O(6)	110.5(3)
S(1)-O(1)	1.461(4)	O(7)#6-Ca(2)-O(6)#1	93.9(2)	O(8)-S(2)-O(7)	110.4(3)
S(1)-O(2)	1.461(5)				
S(1)-O(3)	1.474(4)				
S(1)-O(4)	1.457(5)				
S(2)-O(5)	1.453(5)				
S(2)-O(6)	1.478(5)				
S(2)-O(7)	1.457(5)				
S(2)-O(8)	1.453(5)				

Symmetry transformations used to generate equivalent atoms:(#1) 1−x, 1−y, 1−z; (#2) x, 1.5−y, 0.5+z; (#3) 1+x, 1.5−y, 0.5+z; (#4) 1−x, 2−y, 1−z; (#5) 1−x, −0.5+y, 0.5−z; (#6) −x, −y, −z; (#7) −x, 1−y, −z; (#8) x, −1+y, z; (#9) −x, −0.5+y, 0.5−z; (#10) x, 0.5−y, −0.5+z; (#11) −x, 0.5+y, 0.5−z.

Table S4. Anisotropic displacement parameters for $Cs_2Ca_3(SO_4)_4$.

Atom	U_{11} (Å^2)	U_{22} (Å^2)	U_{33} (Å^2)	U_{23} (Å^2)	U_{13} (Å^2)	U_{12} (Å^2)
Cs1	0.0245(3)	0.0295(3)	0.0202(3)	0.00058(19)	−0.00149(19)	0.00301(19)
Ca1	0.0092(6)	0.0104(6)	0.0132(7)	−0.0012(4)	0.0018(5)	0.0022(5)
Ca2	0.0136(9)	0.0124(8)	0.0155(10)	0.0046(7)	0.0001(7)	−0.0053(7)
S1	0.0098(7)	0.0116(7)	0.0100(7)	−0.0023(5)	0.0042(6)	−0.0005(6)
S2	0.0105(7)	0.0105(7)	0.0094(7)	−0.0017(5)	0.0046(6)	−0.0018(6)
O1	0.014(2)	0.037(3)	0.022(3)	−0.015(2)	0.005(2)	−0.003(2)
O2	0.023(2)	0.025(2)	0.016(3)	−0.008(2)	0.005(2)	0.007(2)
O3	0.019(2)	0.022(2)	0.025(3)	0.0101(19)	0.009(2)	0.005(2)
O4	0.026(3)	0.043(3)	0.014(3)	−0.001(2)	0.010(2)	−0.011(2)
O5	0.020(3)	0.039(3)	0.031(3)	−0.021(2)	0.000(2)	0.012(2)
O6	0.029(3)	0.057(4)	0.022(3)	−0.010(3)	0.019(2)	−0.003(3)
O7	0.056(4)	0.025(3)	0.036(3)	0.015(3)	0.001(3)	−0.021(3)
O8	0.027(3)	0.027(3)	0.012(3)	0.004(2)	−0.001(2)	0.004(2)