Supporting Information

$(CN4H_7)_2SO_4·H_2O$: High-performance Metal-Free Ultraviolet Birefringent Crystal with KBBF-like Configuration

Xia Hao,[*a] Sijing Xie,[a] Ruijie Wang,[a] Chensheng Lin,[b] Lingli Wu,[b] Guang Peng,[c] Tao Yan,[b] Ning Ye[c] and Min Luo[*b]

[a.] *School of Materials Science and Engineering, Henan Normal University, Xinxiang 453007, P. R. China; Email:* hhhaoxia@163.com.

[b.] *Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China.*

[c.] *Tianjin Key Laboratory of Functional Crystal Materials, Institute of Functional Crystal, Tianjin University of Technology, Tianjin 300384, China.*

Table of Contents

Table S1. Atomic coordinates (× 10^4), equivalent isotropic displacement parameters (Å^2 × 10^3) for $(CN_4H_7)_2SO_4 \cdot H_2O$.

Atom	x	y	z	U(eq)
S1	5589.7(10)	2500	5173.8(5)	26.7(2)
O1	6060(4)	2500	6408.2(17)	49.5(6)
O2	7462(3)	2500	4539.4(19)	45.4(6)
O3	4438(3)	1652.9(13)	4886.0(14)	48.5(5)
N1	5329(3)	3850.1(12)	9189.8(15)	33.2(4)
N2	5294(3)	3994.9(11)	7996.2(14)	33.5(4)
N3	4968(3)	4979.3(13)	6458.4(15)	40.8(5)
N4	4992(3)	5594.0(12)	8286.8(15)	37.6(4)
C1	5079(3)	4866.2(13)	7588.4(16)	27.8(4)
O4	3365(3)	7500	7798.4(18)	39.9(5)
H2	5410(30)	3538(13)	7513(17)	37(6)
H3A	4950(50)	5533(11)	6140(20)	53(8)
H3B	5030(50)	4486(14)	6020(20)	53(8)
H4A	5030(40)	5500(20)	9018(9)	49(7)
H4B	4670(40)	6155(10)	8040(20)	47(7)
H1A	6410(30)	3572(19)	9400(20)	54(8)
H1B	4470(40)	3431(18)	9420(20)	61(9)
H4C	2900(60)	7500	7131(16)	57(12)
H4D	2500(60)	7500	8310(30)	89(17)

Table S2. Anisotropic displacement Parameters (Å^2 × 10^3) for $(CN_4H_7)_2SO_4 \cdot H_2O$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U11	U22	U33	U23	U13	U12
S1	38.4(4)	19.9(4)	21.8(4)	0	0.3(2)	0
O1	89.7(18)	34.7(11)	24.1(10)	0	-6.7(11)	0
O2	37.3(11)	57.4(14)	41.5(12)	0	3.1(10)	0
O3	58.2(11)	38.8(10)	48.6(9)	-12.5(7)	3.9(7)	-13.8(8)
N1	44.4(9)	25.3(8)	29.8(8)	4.5(7)	3.2(7)	0.2(7)
N2	51.1(9)	22.0(8)	27.4(8)	-3.0(6)	0.8(7)	1.3(7)
N3	67.2(12)	28.7(10)	26.5(9)	1.2(7)	0.1(8)	-2.4(9)
N4	61.8(11)	22.4(8)	28.6(9)	-0.3(7)	1.1(8)	5.3(8)
C1	29.1(9)	24.9(9)	29.3(9)	1.5(8)	0.9(7)	-2.4(7)
O4	48.3(12)	36.0(11)	35.5(11)	0	0.9(10)	0

Table S3. Bond lengths (Å) and bond angles (°) for $(CN_4H_7)_2SO_4 \cdot H_2O$.

S1-O1	1.474(2)	N1-N2	1.407(2)
S1-O2	1.466(2)	N2-C1	1.329(2)
S1-O3[1]	1.4684(17)	N3-C1	1.330(3)
S1-O3	1.4684(17)	N4-C1	1.314(3)

O2-S1-O1	107.84(15)	O3-S1-O3[1]	109.43(16)
O2-S1-O3[1]	110.04(9)	C1-N2-N1	119.39(16)
O2-S1-O3	110.04(8)	N2-C1-N3	118.19(18)
O3-S1-O1	109.73(9)	N4-C1-N2	120.65(18)
O3[1]-S1-O1	109.73(9)	N4-C1-N3	121.16(18)

1+X, 1/2-Y, +Z

Table S4. Comparison of the optical properties of sulfate in the short-wave UV region.

Number	Compound	Space group	Cutoff edge (nm)	Birefringence	Ref.
1	**$CsSbF_2SO_4$**	***Pna*2$_1$**	**240[a]**	**0.112@1064 nm[d]**	**[1]**
2	$(NH_4)_2Bi_2(SO_4)_2Cl_4$	$P2_12_12_1$	273[c]	0.055@1064 nm[d]	[2]
3	$Rb_2Bi_2(SO_4)_2Cl_4$	$P2_12_12_1$	276[c]	0.047@1064 nm[d]	[2]
4	$K_2Bi_2(SO_4)_2Cl_4$	$P2_12_12_1$	278[c]	0.056@1064 nm[d]	[2]
5	$La(NH_4)(SO_4)_2$	$Pmn2_1$	190[c]	0.03@1064 nm[d]	[3]
6	$ZrF_2(SO_4)$	$Pca2_1$	206[a]	0.074@546 nm[e]	[4]
7	$HfF_2(SO_4)$	$Pca2_1$	190[a]	0.058@546 nm[e]	[4]
8	$CsY(SO_4)_2·4H_2O$	$P2_1/c$	200[c]	0.045@546 nm[d]	[5]
9	$Na_7(IO_3)(SO_4)_3$	$P2_12_12_1$	223[c]	0.085@546 nm[e]	[6]
10	**$NH_3SO_3(NH_4)_2SO_4$**	***Pna*2$_1$**	**218[a]**	**0.104@520 nm[d]**	**[7]**
11	$[C(NH_2)_3]Al(SO_4)_2·6H_2O$	*P*31*m*	<200[c]	0.093@546 nm[e]	[8]
12	$NaRbY_2(SO_4)_4$	*C*2/*c*	200[c]	0.045@ 550 nm[e]	[9]
13	$Bi(SO_4)F·H_2O$	$P2_1/n$	261[c]	0.035@546 nm[e]	[10]
14	$NH_4Y(SO_4)_2·H_2O$	$P2_1/n$	<200[c]	0.022@546.1 nm[e]	[11]
15	$NH_4YSO_4F_2$	$P2_1/m$	210[b]	0.022@546 nm[d]	[11]
16	$Na_2AlSO_4F_3$	*P*2/*c*	<200[c]	0.0076@1064 nm[d]	[12]
17	$Li_4NH_4Al(SO_4)_2F_4$	*C*2/*c*	<200[c]	0.0068@1064 nm[d]	[12]
18	$Li_6K_3Al(SO_4)_4F_4$	*P***Error!**	<200[c]	0.0014@1064 nm[d]	[12]
19	$Na_2(H_2SeO_3)(SO_4)$	$P2_1/c$	210[c]	0.082@1064 nm[d]	[13]
20	**$NaLa(SO_4)_2(H_2O)$**	***P*3$_2$21**	**<192[c]**	**0.13@1064 nm[d]**	**[14]**
21	$[Zn(DETA)_2](SO_4)(H_2O)_3$	*P*1	220[c]	0.045@visible light[e]	[15]
22	$[Zn(H_2O)_6](SO_4)(H_2O)$	$P2_12_12_1$	~200[c]	0.014@1064 nm[d]	[15]
23	$KYSO_4F_2$	$P2_1/m$	< 190[c]	0.015 @564.1 nm[e]	[16]
24	$RbYSO_4F_2$	$P2_1/m$	< 190[c]	0.02@564.1 nm[e]	[16]
25	$RbY(SO_4)_2·4H_2O$	$P2_1/c$	230[c]	0.045@564 nm[d]	[17]
26	$NaK_5La_2(SO_4)_6$	*C*2/*m*	210[c]	0.0245@550 nm[e]	[18]
27	**$(CN_4H_7)_2SO_4·H_2O$**	***Pnma***	**212[c]**	**0.132@546.1 nm[d]**	**This work**

[a]Transmittance spectrum, [b]calculated cut-off edge, [c]diffuse reflection spectrum, [d]calculated birefringence, [e]measured birefringence.

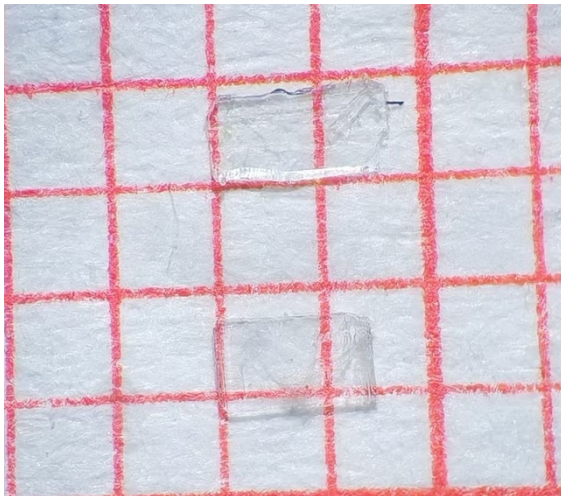

Figure S1. Crystal picture of $(CN_4H_7)_2SO_4 \cdot H_2O$.

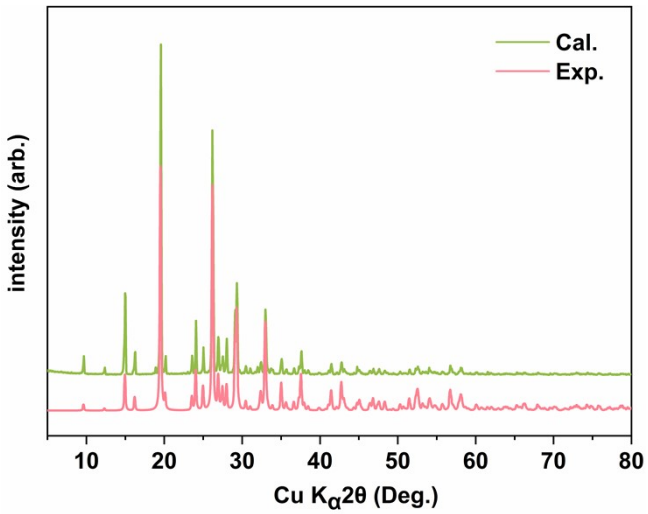

Figure S2. X-ray powder diffraction patterns of $(CN_4H_7)_2SO_4 \cdot H_2O$.

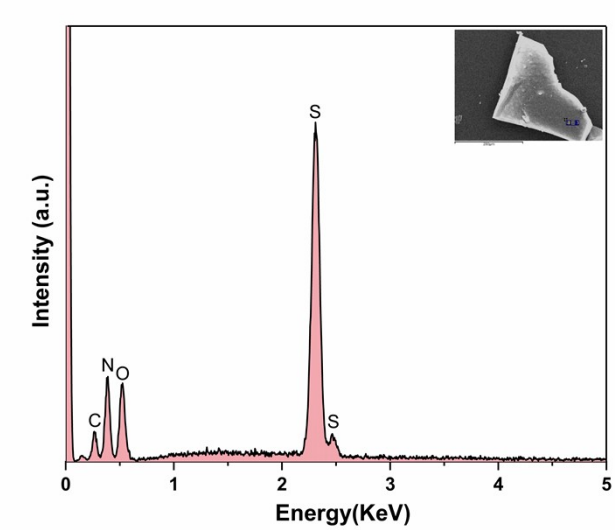

Figure S3. Energy dispersive X-ray spectroscopy analysis of $(CN_4H_7)_2SO_4 \cdot H_2O$.

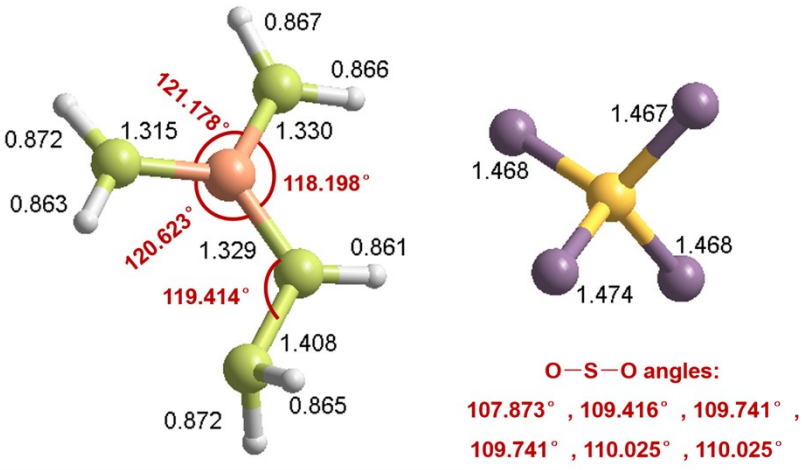

Figure S4. Bond lengths and bond angles of $[CN_4H_7]$, $[SO_4]$ for $(CN_4H_7)_2SO_4{\cdot}H_2O$.

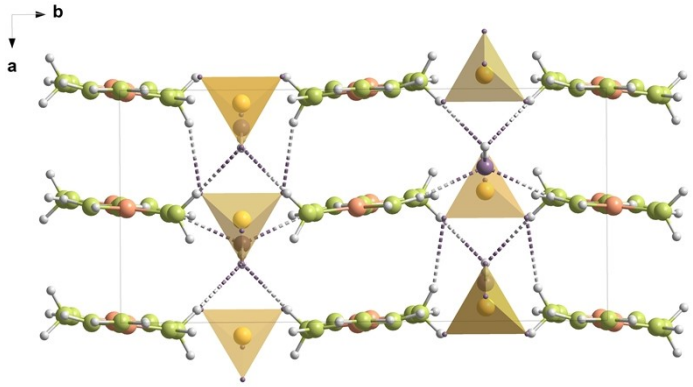

Figure S5. $[(CN_4H_7)_2SO_4{\cdot}H_2O]_\infty$ layers stacking along the a-axis by hydrogen bond.

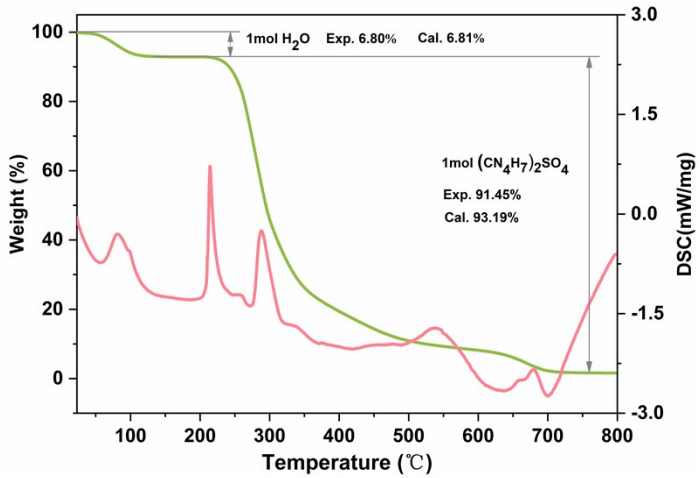

Figure S6. The TG and DSC curves of $(CN_4H_7)_2SO_4{\cdot}H_2O$.

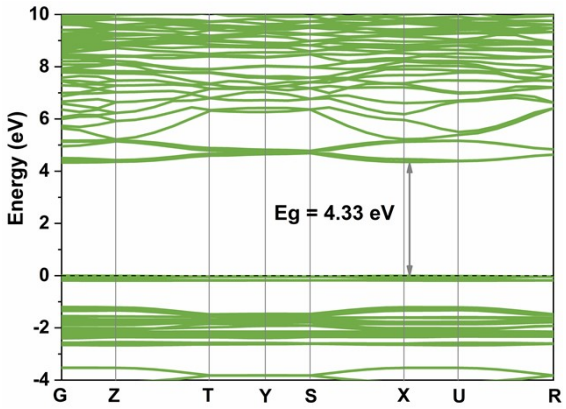

Figure S7. Calculated electronic band structures for $(CN_4H_7)_2SO_4{\cdot}H_2O$.

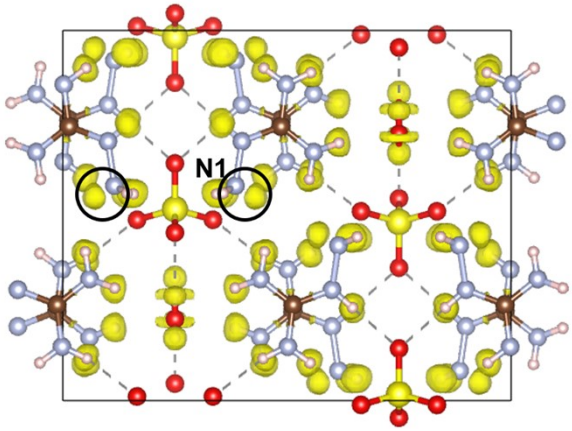

Figure S8. The electron localization function diagram of $(CN_4H_7)_2SO_4{\cdot}H_2O$.

Notes and references

1. X. H. Dong, L. Huang, C. F. Hu, H. M. Zeng, Z. E. Lin, X. Wang, K. M. Ok, G. H. Zou, $CsSbF_2SO_4$: An Excellent Ultraviolet Nonlinear Optical Sulfate with a $KTiOPO_4$ (KTP)-type Structure, Angew. Chem. Int. Ed., 2019, **58**, 6528−6534.
2. K. C. Chen, Y. Yang, G. Peng, S. D. Yang, T. Yan, H. X. Fan, Z. S. Lin, N. Ye, $A_2Bi_2(SO_4)_2Cl_4$ (A = NH_4, K, Rb): achieving a subtle balance of the large second harmonic generation effect and sufficient birefringence in sulfate nonlinear optical materials, J. Mater. Chem. C, 2019, **7**, 9900−9907.
3. C. Wu, X. X. Jiang, Y. L. Hu, C. B. Jiang, T. H. Wu, Z. S. Lin, Z. P. Huang, M. G. Humphrey, C. Zhang, A Lanthanum Ammonium Sulfate Double Salt with a Strong SHG Response and Wide Deep-UV Transparency, Angew. Chem. Int. Ed., 2022, **61**, e202115855.
4. C. Wu, C. B. Jiang, G. F. Wei, X. X. Jiang, Z. J. Wang, Z. S. Lin, Z. P. Huang, M. G. Humphrey, C. Zhang, Toward Large Second-Harmonic Generation and Deep-UV Transparency in Strongly Electropositive Transition Metal Sulfates, J. Am. Chem. Soc., 2023, **145**, 3040−3046.
5. Y. G. Shen, L. J. Huang, Z. F. Wang, Y. W. Zhou, X. L. Xue, H. Lin, R. W. Yan, S. G. Zhao, J. Luo, $CsY(SO_4)_2{\cdot}4H_2O$: A Deep-Ultraviolet Birefringent Crystal Induced by an Edge-Sharing Connection, Inorg. Chem., 2022, **61**, 4468−4475.
6. M. M. Ding, H. W. Yu, Z. G. Hu, J. Y. Wang, Y. C. Wu, $Na_7(IO_3)(SO_4)_3$: the first noncentrosymmetric alkaline-metal iodate-sulfate with isolated [IO_3] and [SO_4] units, Chem. Commun., 2021, **57**, 9598−9601.
7. K. Sudhakar, S. Nandhini, S. Muniyappan, T. Arumanayagam, P. Vivek, P. Murugakoothan, Synthesis, crystal growth, optical, thermal, and mechanical properties of a nonlinear optical single crystal: ammonium sulfate hydrogen sulphamate (ASHS), Appl. Phys. A, 2018, **124**, 334.
8. Y. R. Shang, H. Y. Sha, Z. J. Wang, R. B. Su, C. He, X. M. Yang, X. F. Long, The Birefringence Modulation in Short-Wave Ultraviolet Sulfates with Functional π-Conjugated Cations and Polymerized Heteroleptic Tetrahedral Anions, Adv. Opt. Mater., 2024, **12**, 2302844.

9. Y. Q. Zhao, Y. P. Song, Y. Q. Li, W. Liu, Y. Zhou, W. Q. Huang, J. H. Luo, S. G. Zhao, B. Ahmed, Deep-Ultraviolet Bialkali−Rare Earth Metal Anhydrous Sulfate Birefringent Crystal, Inorg. Chem., 2024, **63**, 11187−11193.

10. J. Lu, Y. Li, Y. Kuk, S. Choi, K. Kim, C. Ko, Z. Bai, K. M. Ok, $Bi(SO_4)F{\cdot}H_2O$ and $Bi(SO_4)(NO_3){\cdot}3H_2O$: Chemical Substitution-Induced Birefringence Enhancement in Bismuth Sulfates, Inorg. Chem., 2024, **63**, 13748−13754.

11. L. Y. Zhang, S. B. Wang, Z. C. Wu, X. L. Hou, Z. H. Yang, F. F. Zhang, S. L. Pan, $NH_4Y(SO_4)_2{\cdot}H_2O$ and $NH_4YSO_4F_2$: Two New Ammonium-Rare Earth Metal Sulfates with Enhanced Optical Anisotropy and Deep Ultraviolet Transmission, Cryst. Res. Technol., 2024, **59**, 2400072.

12. Z. C. Wu, H. M. Li, Z. Y. Zhang, X. Su, H. S. Shi, Y. N. Huang, Design of Deep-Ultraviolet Zero-Order Waveplate Materials by Rational Assembly of $[AlO_2F_4]$ and $[SO_4]$ Groups, Inorg. Chem., 2024, **63**, 1674−1681.

13. X. W. Zhang, Z. X. Wang, C. L. Hu, Y. F. Li, J. G. Mao, F. Kong, UV-Transparent SHG Material Explored in an Alkali Metal Sulfate Selenite System, Inorg. Chem., 2024, **63**, 6067−6074.

14. H. Fu, X. H. Zhang, P. Y. Liu, B. Li, B. L. Wu, Y. Tao, Q. S. Lu, Y. J. Li, J. X. Huang, F. F. Zhang, T. C. He, Z. Chen, H. Wang, C. L. Su, H. Y. Zang, X. J. Yu, X. P. Li, A chiral sodium lanthanum sulfate for second-order nonlinear optics and proton conduction, Inorg. Chem. Front., 2024, **11**, 7026−7033.

15. J. H. Wan, P. Wang, Z. H. Li, C. X. Wu, W. N. Zheng, L. H. Liu, H. M. Liu, Cationic Coordination Modification Drives Birefringence and Nonlinear Effect Double Lifting in Sulfate,Inorg. Chem., 2024, **63**, 24984−24992.

16. Z. C. Wu, H. M. Li, X. L. Hou, Z. H. Yang, H. S. Shi , $AYSO_4F_2$ (A = K, Rb): $[YO_4F_4]$ Polyhedra Enhancement of Birefringence in Non-π-Conjugated Sulfate Systems, Inorg. Chem., 2024, **63**, 4783−4789.

17. W. C. Lu, Y. G. Shen, Q. Wu, $RbY(SO_4)_2{\cdot}4H_2O$: A new ultraviolet birefringent crystal, J. Solid State Chem., 2024, **333**, 124546.

18. L. H. Liu, F. F. Yuan, L. Z. Zhang, Y. S. Huang, Z. B. Lin, $NaK_5La_2(SO_4)_6$: Enhanced Birefringence of Multiple-Alkali Metal Sulfate Systems via Rare Earth Metal-Centered Polyhedra, Inorg. Chem., 2024, **63**, 14721−14726.