Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Dramatically improved optical anisotropy by realizing stereochemcally active lone pairs in a sulfate system, $K_2SO_4 \cdot HIO_3$

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Table S1. Crystal data and structure refinement.

Empirical formula	HIK_2O_7S
Formula weight	350.17
Temperature/K	300.00
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	7.4215(8)
b/Å	7.1578(8)
c/Å	13.8021(15)
β/°	93.330(4)
Volume/Å^3, Z	731.95(14), 4
ρ_{calc} g/cm^3	3.178
μ/mm^{-1}	5.787
F(000)	656.0
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.914 to 56.704
Index ranges	$-9 \leq h \leq 9$, $-9 \leq k \leq 9$, $-18 \leq l \leq 18$
Reflections collected	26266
Independent reflections	1833 [R_{int} = 0.0663, R_{sigma} = 0.0190]
Data/restraints/parameters	1833/2/109
Goodness-of-fit on F^2	1.153
Final R indexes [I>=2σ (I)] [a]	R_1 = 0.0168, wR_2 = 0.0411
Final R indexes [all data] [a]	R_1 = 0.0182, wR_2 = 0.0416
Largest diff. peak/hole / e Å^{-3}	0.85/-0.58

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

Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$). U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
I1	8075.4(2)	3605.4(2)	4522.5(2)	11.76(6)
K1	6688.0(7)	8843.9(7)	5807.7(4)	20.53(11)
K2	989.2(7)	1579.7(7)	6787.8(4)	21.70(11)
S1	5760.4(7)	3504.8(6)	6577.7(4)	12.60(11)
O1	10336.1(18)	2979(2)	4923.7(11)	17.8(3)
O2	5785(2)	3260(2)	7641.6(11)	22.2(3)
O3	7531(2)	2861(2)	6239.3(11)	22.2(3)
O4	5486(2)	5480(2)	6334.2(12)	23.8(3)
O5	4328(2)	2373(2)	6103.5(12)	25.6(4)
O6	8656(2)	4379(2)	3250.9(10)	18.3(3)
O7	7177(2)	1362(2)	4203.3(12)	20.9(3)

Table S3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I1	10.40(8)	12.56(9)	12.30(9)	-0.31(4)	0.49(5)	-0.12(4)
K1	18.8(2)	19.3(2)	23.2(2)	1.45(18)	-0.73(18)	-1.86(17)
K2	17.6(2)	25.3(2)	22.1(2)	7.73(18)	0.06(18)	-1.19(17)
S1	11.7(2)	14.2(2)	12.0(2)	0.39(16)	2.16(18)	-0.76(16)
O1	10.9(7)	23.4(8)	19.1(7)	1.4(6)	0.4(5)	3.8(6)
O2	25.4(8)	28.8(8)	12.5(7)	0.4(6)	3.3(6)	-2.2(7)
O3	15.5(7)	31.2(9)	20.6(8)	4.3(7)	6.7(6)	6.1(6)
O4	25.6(8)	16.3(7)	29.7(9)	6.5(6)	3.5(7)	2.4(6)
O5	22.4(8)	31.5(9)	22.7(8)	-6.2(7)	0.2(6)	-12.0(7)
O6	20.6(7)	22.5(8)	11.9(7)	1.8(6)	3.0(6)	3.8(6)
O7	21.1(8)	14.3(7)	27.5(9)	-3.2(6)	2.0(6)	-4.4(6)

Table S4. Interatomic distances.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I1	O1	1.7929(14)	K1	O5[7]	3.1141(19)
I1	O6	1.9132(15)	K1	O7[7]	2.8943(17)
I1	O7	1.7841(14)	K1	O7[1]	2.8715(17)
S1	O2	1.4779(16)	K2	O1[11]	2.7772(16)
S1	O3	1.4928(15)	K2	O2[10]	2.8498(18)
S1	O4	1.4647(16)	K2	O3[11]	2.7883(16)
S1	O5	1.4608(15)	K2	O4[10]	2.9775(18)
K1	O1[8]	2.8034(15)	K2	O5	2.7614(17)
K1	O2[9]	2.7942(16)	K2	O6[1]	2.9057(18)
K1	O3[7]	2.9955(18)	K2	O6[12]	2.8288(16)
K1	O4	2.6825(16)	K2	O7[13]	2.8936(17)
K1	O5[1]	2.8379(16)			

[1]1-X, 1-Y, 1-Z; [2]+X, -1+Y, +Z; [3]1/2+X, 1/2-Y, -1/2+Z; [4]1+X, +Y, +Z; [5]1-X, 2-Y, 1-Z; [6]1+X, 1+Y, +Z; [7]+X, 1+Y, +Z; [8]2-X, 1-Y, 1-Z; [9]3/2-X, 1/2+Y, 3/2-Z; [10]1/2-X, -1/2+Y, 3/2-Z; [11]-1+X, +Y, +Z; [12]-1/2+X, 1/2-Y, 1/2+Z; [13]1-X, -Y, 1-Z.

Table S5. Bond angles.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O7	I1	O1	100.41(7)	$O1^{10}$	K2	$O2^{12}$	23.24(3)
O7	I1	O6	97.74(7)	$O1^{10}$	K2	$O3^{10}$	76.44(3)
$O1^{8}$	K1	$O3^{7}$	63.442(15)	$O1^{10}$	K2	$O4^{12}$	141.44(4)
$O1^{8}$	K1	$O5^{1}$	120.04(2)	$O1^{10}$	K2	$O6^{1}$	119.88(5)
$O1^{8}$	K1	$O5^{7}$	165.400(17)	$O1^{10}$	K2	$O6^{13}$	61.41(4)
$O1^{8}$	K1	$O7^{1}$	105.171(16)	$O1^{10}$	K2	$O7^{14}$	148.06(5)
$O1^{8}$	K1	$O7^{7}$	67.793(17)	$O2^{12}$	K2	$O4^{12}$	106.43(4)
$O2^{9}$	K1	$O1^{8}$	66.339(15)	$O2^{12}$	K2	$O6^{1}$	45.45(3)
$O2^{9}$	K1	$O3^{7}$	118.07(4)	$O2^{12}$	K2	$O7^{14}$	24.77(3)
$O2^{9}$	K1	$O5^{7}$	121.20(4)	$O3^{10}$	K2	$O2^{12}$	38.33(3)
$O2^{9}$	K1	$O5^{1}$	73.37(3)	$O3^{10}$	K2	$O4^{12}$	49.62(4)
$O2^{9}$	K1	$O7^{1}$	135.21(4)	$O3^{10}$	K2	$O6^{1}$	90.69(4)
$O2^{9}$	K1	$O7^{7}$	111.01(5)	$O3^{10}$	K2	$O6^{13}$	85.22(5)
$O3^{7}$	K1	$O5^{7}$	72.23(5)	$O3^{10}$	K2	$O7^{14}$	86.80(5)
O4	K1	$O1^{8}$	152.33(5)	O5	K2	$O1^{10}$	58.79(4)
O4	K1	$O2^{9}$	141.43(5)	O5	K2	$O2^{12}$	135.55(4)
O4	K1	$O3^{7}$	82.99(5)	O5	K2	$O3^{10}$	137.08(4)
O4	K1	$O5^{7}$	125.35(4)	O5	K2	$O4^{12}$	73.79(5)
O4	K1	$O5^{1}$	160.32(4)	O5	K2	$O6^{1}$	134.75(5)
O4	K1	$O7^{7}$	46.62(4)	O5	K2	$O6^{13}$	132.03(5)
O4	K1	$O7^{1}$	92.53(4)	O5	K2	$O7^{14}$	137.27(5)
$O5^{1}$	K1	$O3^{7}$	72.44(5)	$O6^{13}$	K2	$O2^{12}$	124.34(3)
$O5^{1}$	K1	$O5^{7}$	82.42(5)	$O6^{1}$	K2	$O4^{12}$	69.74(3)
$O5^{1}$	K1	$O7^{1}$	112.25(5)	$O6^{13}$	K2	$O4^{12}$	133.11(3)
$O5^{1}$	K1	$O7^{7}$	142.78(5)	$O6^{13}$	K2	$O6^{1}$	85.17(5)
$O7^{1}$	K1	$I1^{1}$	124.80(5)	$O6^{13}$	K2	$O7^{14}$	108.50(4)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O7[1]	K1	O3[7]	110.17(4)	O7[14]	K2	O4[12]	108.47(4)
O7[7]	K1	O3[7]	129.21(4)	O7[14]	K2	O6[1]	82.48(3)
O7[7]	K1	O5[7]	133.09(4)	O2	S1	O3	150.76(2)
O7[1]	K1	O5[7]	87.78(5)	O4	S1	O2	140.45(7)
O7[1]	K1	O7[7]	82.95(5)	O4	S1	O3	149.08(7)
O5	S1	O3	59.84(7)	O5	S1	O2	109.83(10)
O5	S1	O4	110.74(7)				

[1]1-X, 1-Y, 1-Z; [2]+X, -1+Y, +Z; [3]1/2+X, 1/2-Y, -1/2+Z; [4]1+X, +Y, +Z; [5]1-X, 2-Y, 1-Z; [6]1+X, 1+Y, +Z; [7]+X, 1+Y, +Z; [8]2-X, 1-Y, 1-Z; [9]3/2-X, 1/2+Y, 3/2-Z; [10]-1+X, +Y, +Z; [11]-1+X, -1+Y, +Z; [12]1/2-X, -1/2+Y, 3/2-Z; [13]-1/2+X, 1/2-Y, 1/2+Z; [14]1-X, -Y, 1-Z; [15]1/2-X, 1/2+Y, 3/2-Z; [16]3/2-X, -1/2+Y, 3/2-Z.

Table S6. Hydrogen Bonds.

D H A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O3 H3 O7	1.00(2)	2.19(8)	3.005(2)	138(9)
O6 H6 O2[1]	0.958(18)	1.680(18)	2.631(2)	172(3)

[1]1/2+X, 1/2-Y, -1/2+Z[1]1-X, 1-Y, 1-Z; [2]2-X, 1-Y, 1-Z; [3]+X, -1+Y, +Z; [4]1+X, +Y, +Z; [5]1-X, -Y, 1-Z; [6]3/2-X, -1/2+Y, 3/2-Z; [7]1/2-X, 1/2+Y, 3/2-Z; [8]1/2+X, 1/2-Y, -1/2+Z.

Table S7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3).

Atom	*x*	*y*	*z*	U(eq)
H3	7020(130)	1950(130)	5750(70)	30(30)
H6	9440(40)	3480(40)	2970(20)	13(8)

Table S8. Atomic Occupancy.

Atom	*Occupancy*	Atom	*Occupancy*
H3	0.25	H6	0.75

Table S9. The bond valence sum (BVS) calculated by PLATON.

Atom	**BVS**	**Atom**	**BVS**
I1	+4.843	O3	-1.958
S1	+5.995	O4	-1.867
K1	+1.135	O5	-1.954
K2	+1.175	**O6**	**-1.548**
O1	-2.102	O7	-2.196
O2	**-1.795**		

Table S10. The (*hkl*) index of (001)-oriented single crystal slices for refractive indices measurement.

(*hkl*)	observed 2θ /°	calculated 2θ/°
(00-2)	12.840	12.839
(00-4)	25.840	25.843
(00-8)	53.140	53.133

Table S11. The measured refractive index of $K_2SO_4 \cdot HIO_3$ on gem refractometer at 589.3 nm.

Rotation angle/°	0	45	90	135	180	225	270	315
n_1	**1.535 (min)**	1.55	1.60	1.60	1.60	1.62	1.61	1.565
n_2	1.61	1.61	1.64	1.65	1.66	**1.675 (max)**	1.65	1.62

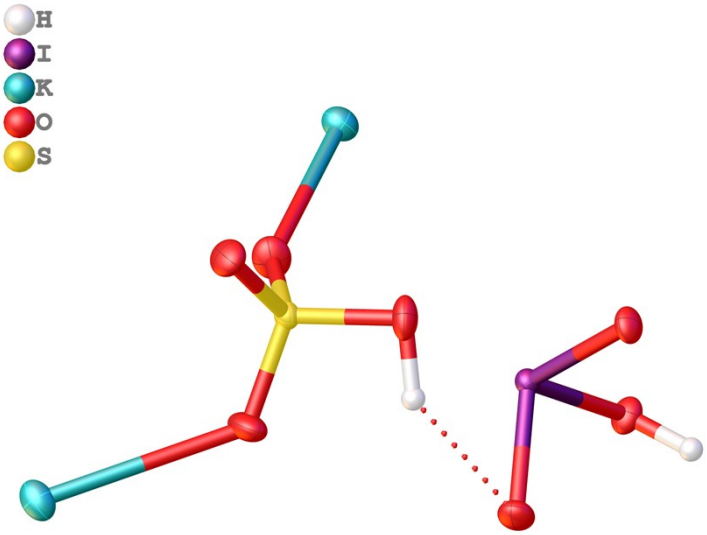

Fig. S1 Asymmetric unit of $K_2SO_4 \cdot HIO_3$.

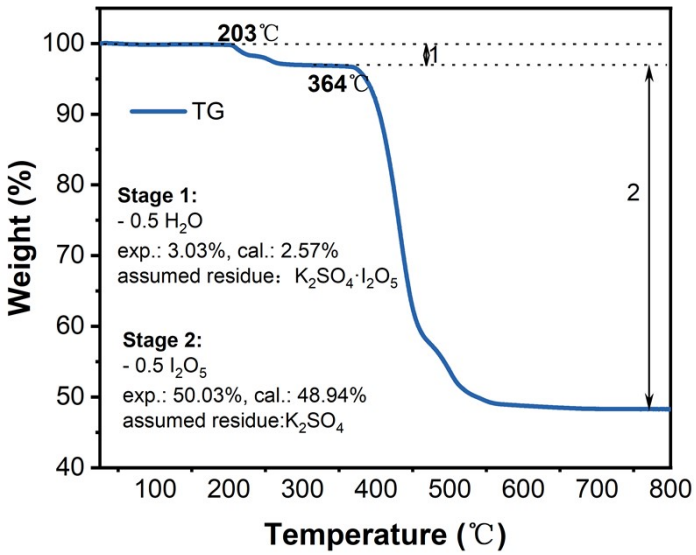

Fig. S2 The TGA diagram of $K_2SO_4 \cdot HIO_3$.

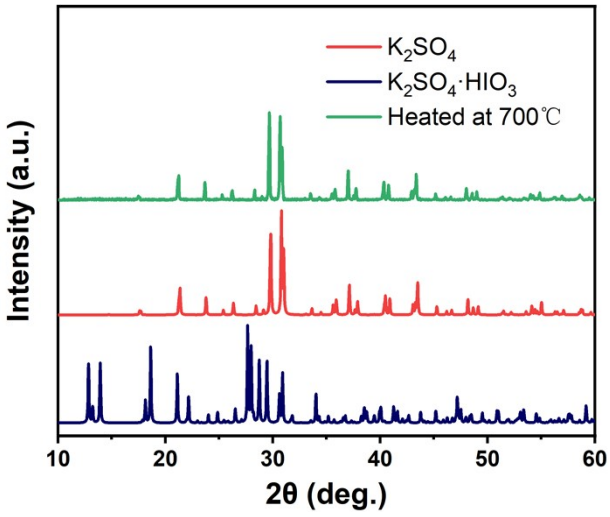

Fig. S3 PXRD patterns of $K_2SO_4 \cdot HIO_3$ measure before and after heating at 700 ℃.

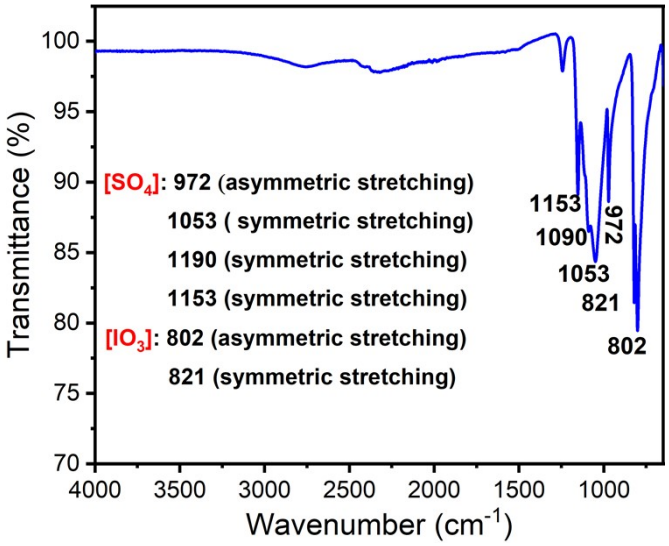

Fig. S4 The FT-IR spectrum of $K_2SO_4 \cdot HIO_3$.

The asymmetric stretching vibration of $[SO_4]$ was found at 972 cm^{-1} while the symmetric stretching vibrations for $[SO_4]$ occurred at 1053, 1153, and 1190 cm^{-1}. In addition, peaks occurring at 802 and 821 cm^{-1} could be assigned to the asymmetric and symmetric stretching vibrations of $[IO_3]$, respectively.

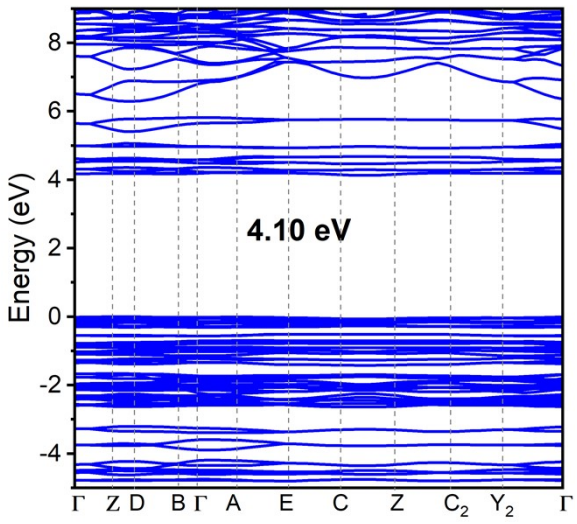

Fig. S5 The calculated band structure of $K_2SO_4 \cdot HIO_3$.

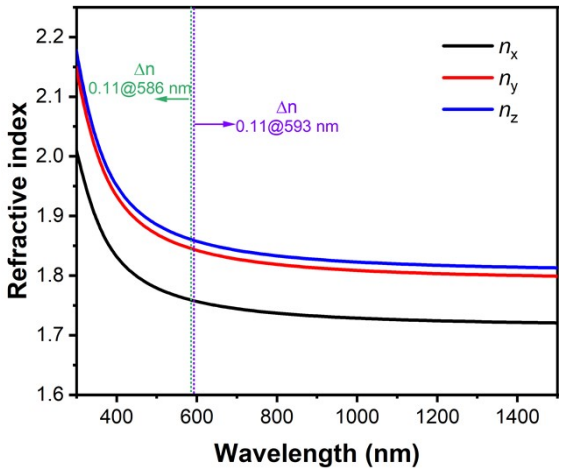

Fig. S6 The calculated refractive index curves of $K_2SO_4 \cdot HIO_3$ based on DFT theory.