Supporting Information

$K_2S_4O_6$: improving birefringence and nonlinear optical property with $[O_3S\text{-}S\text{-}S\text{-}SO_3]^{2-}$ group

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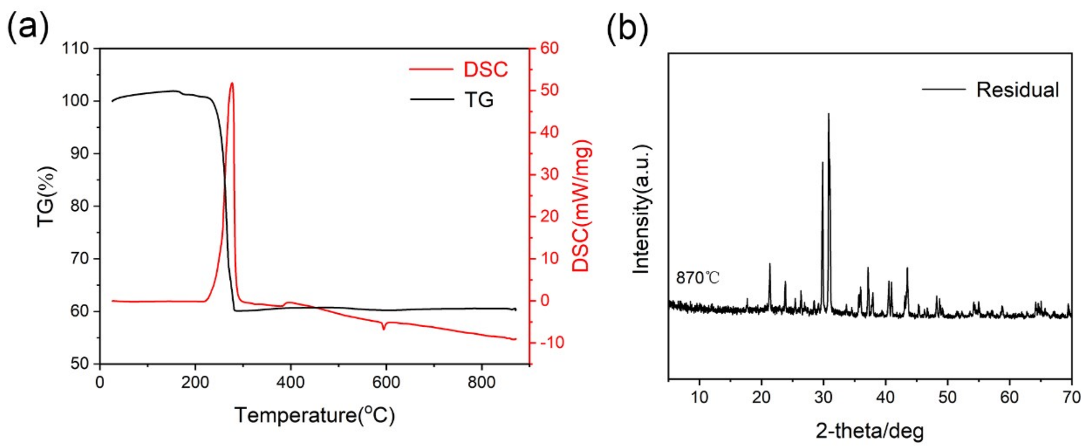


Figure S1. (a) The thermogravimetric (TG) and differential scanning calorimetry (DSC) curves of $K_2S_4O_6$. (b) The PXRD pattern of residual.

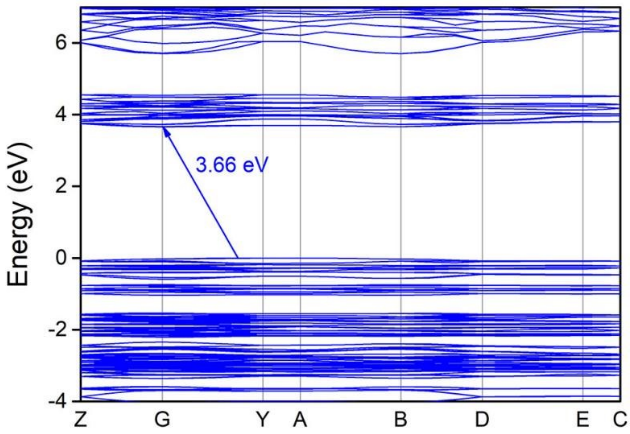


Figure S2. The calculated band structure structure of $K_2S_4O_6$.

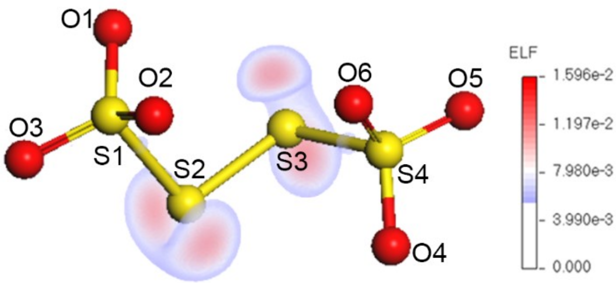


Figure S3. The electron localization function (ELF) of $K_2S_4O_6$.

Table S1. The SHG response, birefringence, and band gap of sulfate NLO materials.

Compounds	SHG (×KDP)	Birefringence	E_g	E_g(Calc.)	Ref.
LiNaSO4	1.09	N/A	3.5	N/A	[1]
LiKSO4	3	N/A	4.9	N/A	[2]
$Li_2SO_4\cdot H_2O$	<1	0.023	4.89	N/A	[3]
$Rb_2Mg_2(SO_4)_3$	0.3	N/A	>6.2	6.05	[4]
$Rb_2Ca_2(SO_4)_3$	0.3	N/A	<200	N/A	[5]
$Cs_2Ca_2(SO_4)_3$	0.6	N/A	6.2	5.95	[6]
$Cs_2Mg_3(SO_4)_4$	0.4	N/A	<200	N/A	[7]
$Li_8NaRb_3(SO_4)_6\cdot 2H_2O$	0.5	N/A	N/A	4.86	[8]
$NH_4NaLi_2(SO_4)_2$	1.1	N/A	<186nm	N/A	[9]
$(NH_4)_2Na_3Li_9(SO_4)_7$	0.5	N/A	<190nm	N/A	[9]
$Li_9Na_3Rb_2(SO_4)_7$	1.3	N/A	6.70	N/A	[10]
$CsSbF_2SO_4$	3	0.112	4.76	4.33	[11]
$RbSbCl_2SO_4$	2.7	N/A	N/A	3.48	[12]
$K_2Bi_2(SO_4)_2Cl_4$	5.5	0.056	4.46	3.91	[13]
$(NH_4)_2Bi_2(SO_4)_2Cl_4$	4.8	0.055	5.54	3.94	[13]
$Rb_2Bi_2(SO_4)_2Cl_4$	5.3	0.047	4.49	3.94	[13]
$Ce(SO_4)F_2$	8	0.361@546 nm	2.71	1.23	[14]
$Te(CS(NH_2)_2)_4SO_4\cdot 2H_2O$	2.4	0.21@546.1 nm	3	2.949	[15]
$Mg[CS(NH_2)_2]_3SO_4$	0.83	N/A	5.25	N/A	[16]
$Zn[CS(NH_2)_2]_3SO_4$	1.2	0.16@554 nm	4.96	N/A	[17]
$(C_6H_5NH_3)HSO_4$	0.4*Urea	N/A	4.9	N/A	[18]
$Cs_2Zn_2(SO_4)_3$	0.15	N/A	3.49	4.46	[4]
$RbSbF_2SO_4$	0.96	N/A	4.75	4.62	[19]
$(NH_4)SbCl_2SO_4$	1.7	N/A	4.54	4.12	[20]
$[Ag(NH_3)_2]_2SO_4$	1.4	0.102	4.42	2.93	[21]
$KBiCl_2SO_4$	1.7	0.098	3.95	4.34	[22]
$KTb(SO_4)_2$	0.3	0.019	3.04	N/A	[23]
$Sb_4O(SO_4)(OH)_2$	1.2	0.147	3.46	4.41	[24]
$K_2Zn_3(SO_4)(HSO_4)_2F_4$	0.3	0.0126@546 nm	N/A	6.53	[25]
$Te_2O_3SO_4$	6	0.043@546.1 nm	4.24	1.954	[26]
$Te(OH)_3(SO_4)\cdot H_3O$	3	0.052@546.1 nm	4.72	4.538	[26]
$K_2SO_4\cdot SbF_3$	0.1	N/A	4.44	N/A	[27]
$Rb_2SO_4\cdot SbF_3$	0.3	N/A	4.15	4.16	[27]
$Y_2(Te_4O_{10})(SO_4)$	N/A	0.149@532 nm	4.1	3.66	[28]
$Y_3(TeO_3)_2(SO_4)_2(OH)(H_2O)$	N/A	0.092@532 nm	4.4	1.71	[28]

N/A = not reported or not available.

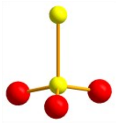
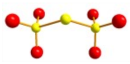
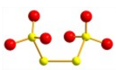
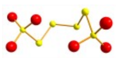
Table S2. The Mulliken population of bonds in $K_2S_4O_6$.

Bond	Population	Length(A)
S1-O1	0.55	1.47695
S1-O2	0.57	1.46362
S1-O3	0.56	1.47057
S1-S2	0.36	2.15969
S2-S3	0.39	2.01894
S3-S4	0.36	2.17330
S4-O4	0.56	1.46830
S4-O5	0.57	1.45955
S4-O6	0.57	1.46436

Table S3. The chemical formula, space group, band gap Eg-GGA and birefringence Δn at 1064 nm (without scissors correction), of different sulfates, thiosulfates and polythionates.

Crystals	Space group	Units	Band gap (eV)	Birefringence (@1064 nm)
$LiNaSO_4$	*P*3*c*	SO_4	5.589	0.006
$LiKSO_4$	*P*3*c*	SO_4	5.279	0.001
$Li_2SO_4.H_2O$	$P2_1$	SO_4	4.89	0.023
$Na_2S_2O_3$	$P2_1/a$	S_2O_3	4.197	0.121
$Na_2S_2O_3$	$Pna2_1$	S_2O_3	4.088	0.027
$K_2(S_2O_3)$	$P2_1/c$	S_2O_3	3.639	0.091
$Cs_2(S_2O_3)$	$P2_1/c$	S_2O_3	3.881	0.109
$K_2(S_3O_6)$	*Pnam*	S_3O_6	3.562	0.146
$K_2(S_4O_6)$	*Cc*	S_4O_6	3.749	0.065
$Na_2(S_4O_6)\cdot 2H_2O$	$C2_1$	S_4O_6	3.769	0.204
$K_2Ba(S_6O_6)_2$	*P*2/*c*	S_6O_6	2.743	0.206

Table S4. Structures, polarizability (α), polarizability anisotropy (δ), hyperpolarizability (β), and HOMO–LUMO gap (E_g) of $(SO_4)^{2-}$, $(SO_3S)^{2-}$, $(S_3O_6)^{2-}$, $(S_4O_6)^{2-}$, and $(S_6O_6)^{2-}$.

Groups	Structures	α	diagonalized α	δ	β	Eg (eV)
SO_4^{2-}		$\alpha_{xx}=\alpha_{yy}=\alpha_{zz}$=32.25	$\alpha_{xx}=\alpha_{yy}=\alpha_{zz}$= 32.25	0	β_{xxx}=−3.16, $\beta_{xyy}=\beta_{xzz}$=1.58, $\beta_{yzz}=-\beta_{yyy}$=2.24	7.40
$S_2O_3^{2-}$		$\alpha_{xx}=\alpha_{yy}$=30.26 α_{zz}=57.67	$\alpha_{xx}=\alpha_{yy}$=30.26 α_{zz}=57.67	27.41	$\beta_{xxy}=-\beta_{yyy}$=10.21, $\beta_{xxz}=\beta_{yyz}$=29.40, β_{zzz}=213.15	6.21
$S_3O_6^{2-}$		α_{xx}=85.40, α_{xy}=−16.36, α_{yy}=80.34, α_{zz}=52.33	α_{xx}=52.33 α_{yy}=66.32 α_{zz}=99.43	47.10	β_{xxx}=58.79, β_{xxy}=10.31, β_{xyy}=33.69, β_{yyy}=73.74, β_{xzz}=21.20, β_{yzz}=35.75	6.27
$S_4O_6^{2-}$		α_{xx}=83.35, α_{xy}=13.22, α_{yy}=112.47, α_{xz}=5.38, α_{yz}=14.48, α_{zz}=73.07	α_{xx}=68.23 α_{yy}=78.24 α_{zz}=122.41	54.18	β_{xxx}=113.94, β_{xxy}=−32.61, β_{xyy}=19.75, β_{yyy}=17.70, β_{xxz}=−9.51, β_{xyz}=−10.81, β_{yyz}=15.93, β_{xzz}=42.85, β_{yzz}=−4.84, β_{zzz}=3.91	5.54
$S_6O_6^{2-}$		α_{xx}=111.89, α_{xy}=−14.24, α_{yy}=116.49, α_{xz}=8.62, α_{yz}=9.73, α_{zz}=155.70	α_{xx}=96.94 α_{yy}=128.52 α_{zz}=158.63	61.69	β_{xxx}=113.99, β_{xxy}=−60.05, β_{xyy}=62.65, β_{yyy}=−124.19, β_{xxz}=−6.83, β_{xyz}=8.66, β_{yyz}=3.66, β_{xzz}=107.39, β_{yzz}=−115.94, β_{zzz}=104.76	4.59

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