Supporting Information

$Li_8NaRb_3(SO_4)_6{\cdot}2H_2O$ as a new sulfate deep-ultraviolet nonlinear optical material†

Yanqiang Li,[abc] Sangen Zhao,*[a] Pai Shan,[a] Xianfeng Li,[ab] Qingran Ding,[ab] Shuai Liu,[ab] Zhenyue Wu,[ab] Sasa Wang,[ab] Lina Li,[a] and Junhua Luo*[a]

Contents

[a] *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China.*
**E-mail: zhaosangen@fjirsm.ac.cn, jhluo@fjirsm.ac.cn*
[b] *University of the Chinese Academy of Sciences, Beijing 100049, China.*
[c] *School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China.*

† Electronic supplementary information (ESI) available: CIF file; Elemental analysis; Powder XRD patterns of the samples before and after TG/DSC test; Coordination environments for Na and Rb; Atomic coordinates and equivalent isotropic displacement parameters; Anisotropic displacement parameters; Selected bond distances and angles; CCDC-number 1832967 for $Li_8NaRb_3(SO_4)_6{\cdot}2H_2O$. See DOI: 10.1039/x0xx00000x.

Elemental analysis for $Li_8NaRb_3(SO_4)_6 \cdot 2H_2O$

The elemental analysis of $Li_8NaRb_3(SO_4)_6 \cdot 2H_2O$ was performed with a Jobin Yvon Ultima2 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). In the measurement, the $Li_8NaRb_3(SO_4)_6 \cdot 2H_2O$ samples were dissolved in nitric acid at the boiling point for 1 h. According to the results of the elemental analysis, the experimental ratio of Li: Na: Rb: S (8.5: 0.9: 2.7: 5.8) agrees well with the compositions from the single-crystal data analysis.

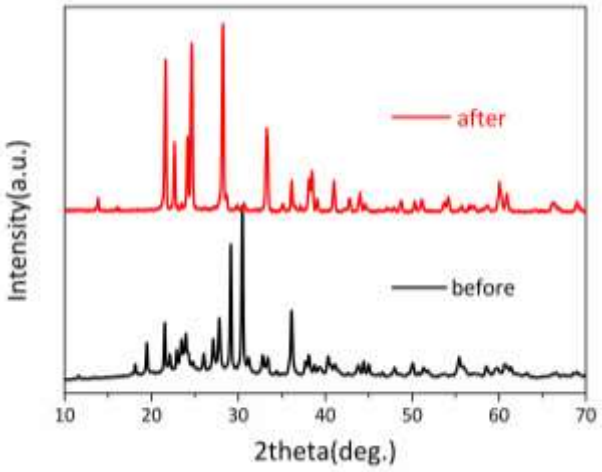

Fig. S1. The powder XRD patterns of the samples before TG/DSC test and after TG/DSC test.

We have performed the powder XRD measurements for the samples after TG/DSC tests (**Fig.** S1). However, there are not matching XRD patterns in the XRD PDF database.

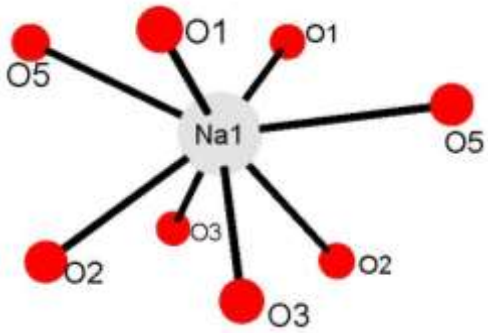

Fig. S2. Coordination environments for Na1 in the structure of $Li_8NaRb_3(SO_4)_6 \cdot 2H_2O$.

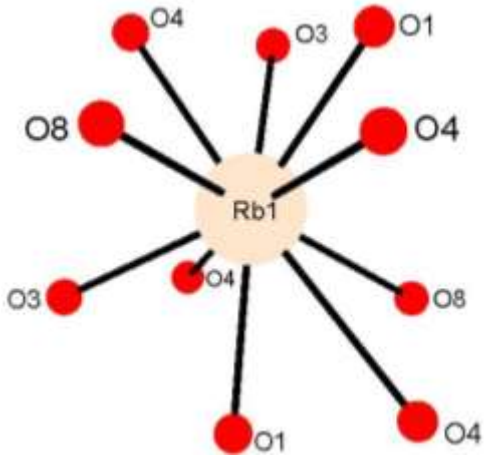

Fig. S3. Coordination environments for Rb1 in the structure of $Li_8NaRb_3(SO_4)_6 \cdot 2H_2O$.

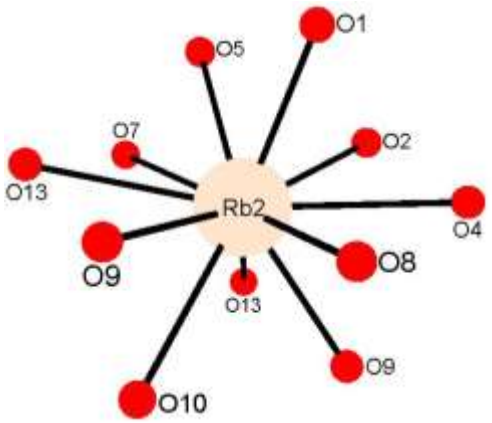

Fig. S4. Coordination environments for Rb2 in the structure of $Li_8NaRb_3(SO_4)_6 \cdot 2H_2O$.

Table S1. Atomic coordinates and equivalent isotropic displacement parameters for $Li_8NaRb_3(SO_4)_6 \cdot 2H_2O$.

Atom	*Wyck.*	*Site*	*x/a*	*y/b*	*z/c*	*Ueq*(Å^2)
Rb1	2a	2	1/2	0.8833(3)	1/2	0.0252(4)
Rb2	4c	1	0.63194(4)	0.9099(3)	1.39265(16)	0.0485(4)
S1	4c	1	0.46019(7)	0.3887(6)	0.6889(3)	0.0185(5)
S2	4c	1	0.61506(7)	0.8839(6)	0.8530(3)	0.0182(5)
S3	4c	1	0.78589(7)	0.8963(6)	1.7734(2)	0.0169(5)
Na1	2b	2	1/2	0.1570(15)	1/2	0.074(3)
O1	4c	1	0.4634(3)	0.0934(15)	0.6661(10)	0.0273(17)
O2	4c	1	0.4318(2)	0.5045(14)	0.5372(9)	0.0218(15)
O3	4c	1	0.5068(2)	0.5077(15)	0.7140(9)	0.0249(17)
O4	4c	1	0.4401(2)	0.4539(15)	0.8285(9)	0.0276(18)
O5	4c	1	0.5849(3)	1.0035(15)	0.7094(9)	0.0271(17)
O6	4c	1	0.6056(2)	0.5898(14)	0.8561(9)	0.0215(15)
O7	4c	1	0.6627(2)	0.9227(18)	0.8359(9)	0.0289(17)
O8	4c	1	0.6079(3)	1.0037(15)	1.0082(10)	0.0284(17)
O9	4c	1	0.8343(2)	0.9549(15)	1.7794(9)	0.0251(17)
O10	4c	1	0.7784(2)	0.6003(15)	1.7782(9)	0.0226(16)
O11	4c	1	0.7590(2)	1.0033(15)	1.6168(9)	0.0245(16)
O12	4c	1	0.7697(2)	1.0155(14)	1.9169(9)	0.0227(16)
O13	4c	1	0.68320(17)	0.3898(16)	1.6538(6)	0.0129(11)
Li1	4c	1	0.7836(5)	0.396(5)	1.9880(19)	0.025(3)
H13A	4c	1	0.6808	0.3351	1.7556	0.03
H13B	4c	1	0.6586	0.3256	1.5877	0.03
Li2	4c	1	0.7392(5)	0.391(5)	1.611(2)	0.029(3)
Li3	4c	1	0.6089(5)	1.386(5)	1.061(2)	0.030(3)
Li4	4c	1	0.4333(5)	0.393(6)	0.3125(19)	0.025(3)

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

Table S2. Anisotropic displacement parameters (Å^2) for $Li_8NaRb_3(SO_4)_6 \cdot 2H_2O$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rb1	0.0307(7)	0.0223(7)	0.0203(6)	0.00000	0.0006(5)	0.00000
Rb2	0.0527(7)	0.0452(8)	0.0502(8)	-0.0044(9)	0.0146(6)	-0.0013(8)
S1	0.0186(10)	0.0174(11)	0.0196(11)	0.0013(13)	0.0035(8)	0.0010(13)
S2	0.0181(10)	0.0157(11)	0.0205(11)	0.0008(12)	0.0025(8)	0.0012(12)
S3	0.0177(10)	0.0166(11)	0.0166(10)	0.0011(13)	0.0028(8)	0.0003(12)
Na1	0.173(11)	0.020(4)	0.047(5)	0.00000	0.067(6)	0.00000
O1	0.032(4)	0.017(3)	0.030(4)	0.001(3)	-0.002(3)	0.003(3)
O2	0.024(4)	0.022(3)	0.018(4)	0.007(3)	-0.003(3)	0.000(3)
O3	0.018(3)	0.033(4)	0.025(4)	-0.001(3)	0.004(3)	-0.005(3)
O4	0.032(4)	0.023(5)	0.030(4)	-0.006(3)	0.011(3)	-0.009(3)
O5	0.035(4)	0.020(3)	0.022(4)	0.005(3)	-0.006(3)	0.004(3)
O6	0.027(4)	0.016(3)	0.021(4)	-0.002(3)	0.005(3)	-0.002(3)
O7	0.018(3)	0.032(4)	0.036(4)	-0.007(4)	0.005(3)	0.015(4)
O8	0.036(4)	0.025(4)	0.027(4)	-0.005(3)	0.013(3)	-0.008(3)
O9	0.017(3)	0.026(4)	0.030(4)	0.004(3)	0.001(3)	0.004(3)
O10	0.029(4)	0.017(3)	0.022(4)	0.002(3)	0.005(3)	0.003(3)
O11	0.026(4)	0.025(4)	0.019(4)	0.009(3)	-0.001(3)	0.001(3)
O12	0.030(4)	0.021(4)	0.020(4)	-0.001(3)	0.011(3)	-0.001(3)
O13	0.014(3)	0.010(3)	0.011(3)	0.000(3)	-0.005(2)	-0.005(3)

Table S3. Selected bond distances (Å) and angles (deg.) for $Li_8NaRb_3(SO_4)_6 \cdot 2H_2O$.

Selected bonds	Distances (Å)	Selected angles	Angles (deg.)
Rb(1)-O(1)^{i}	2.936(8)	**O(4)-S(1)-O(2)**	108.8(5)
Rb(1)-O(1)^{ii}	2.936(8)	**O(4)-S(1)-O(1)**	111.8(5)
Rb(1)-O(4)	2.957(7)	**O(2)-S(1)-O(1)**	108.7(4)
Rb(1)-O(4)^{iii}	2.957(7)	**O(4)-S(1)-O(3)**	108.8(4)
Rb(1)-O(3)	3.027(8)	**O(2)-S(1)-O(3)**	109.7(5)
Rb(1)-O(3)^{iii}	3.027(8)	**O(1)-S(1)-O(3)**	109.0(5)
Rb(1)-O(8)	3.261(8)	**O(8)-S(2)-O(5)**	111.6(5)
Rb(1)-O(8)^{iii}	3.261(8)	**O(8)-S(2)-O(7)**	109.6(5)
Rb(1)-O(4)^{i}	3.494(8)	**O(5)-S(2)-O(7)**	109.2(5)
Rb(1)-O(4)^{ii}	3.494(8)	**O(8)-S(2)-O(6)**	109.0(5)
Rb(2)-O(2)^{iii}	2.893(7)	**O(5)-S(2)-O(6)**	108.6(4)
Rb(2)-O(9)^{iv}	2.935(8)	**O(7)-S(2)-O(6)**	108.8(5)
Rb(2)-O(1)^{i}	2.940(8)	**O(9)-S(3)-O(12)**	111.3(4)
Rb(2)-O(8)	3.125(8)	**O(9)-S(3)-O(11)**	109.3(4)
Rb(2)-O(5)^{v}	3.206(8)	**O(12)-S(3)-O(11)**	109.9(4)
Rb(2)-O(9)^{vi}	3.288(8)	**O(9)-S(3)-O(10)**	110.3(4)
Rb(2)-O(13)^{ii}	3.362(7)	**O(12)-S(3)-O(10)**	107.5(4)
Rb(2)-O(10)^{vi}	3.377(8)	**O(11)-S(3)-O(10)**	108.5(4)
Rb(2)-O(4)^{iii}	3.397(8)	**O(7)^{iv}-Li(1)-O(10)**	121.8(10)
Rb(2)-O(13)	3.510(7)	**O(7)^{iv}-Li(1)-O(12)^{xiv}**	107.3(8)
Rb(2)-O(7)^{v}	3.571(8)	**O(10)-Li(1)-O(12)^{xiv}**	105.2(9)
S(1)-O(4)	1.428(7)	**O(7)^{iv}-Li(1)-O(12)^{viii}**	111.7(10)
S(1)-O(2)	1.478(7)	**O(10)-Li(1)-O(12)^{viii}**	104.4(8)
S(1)-O(1)	1.479(8)	**O(12)^{xiv}-Li(1)-O(12)^{viii}**	105.1(8)
S(1)-O(3)	1.487(7)	**O(13)-Li(2)-O(10)**	109.5(10)
S(2)-O(8)	1.457(8)	**O(13)-Li(2)-O(11)^{iv}**	112.8(9)
S(2)-O(5)	1.465(8)	**O(10)-Li(2)-O(11)^{iv}**	113.6(11)
S(2)-O(7)	1.466(7)	**O(13)-Li(2)-O(11)^{viii}**	106.0(11)
S(2)-O(6)	1.483(8)	**O(10)-Li(2)-O(11)^{viii}**	111.0(9)
S(3)-O(9)	1.465(7)	**O(11)^{iv}-Li(2)-O(11)^{viii}**	103.6(9)
S(3)-O(12)	1.469(7)	**O(4)^{i}-Li(3)-O(8)**	107.6(11)
S(3)-O(11)	1.476(7)	**O(4)^{i}-Li(3)-O(6)^{ii}**	113.5(11)
S(3)-O(10)	1.483(8)	**O(8)-Li(3)-O(6)^{ii}**	109.1(9)
Na(1)-O(1)^{ix}	2.266(9)	**O(4)^{i}-Li(3)-O(9)^{vi}**	107.1(9)
Na(1)-O(1)	2.266(9)	**O(8)-Li(3)-O(9)^{vi}**	107.1(10)

Na(1)-O(3)^{xi}	2.396(9)	**O(6)^{ii}-Li(3)-O(9)^{vi}**	112.2(10)
Na(1)-O(3)^{viii}	2.396(9)	**O(6)^{ix}-Li(4)-O(3)^{ix}**	102.8(11)
Na(1)-O(2)^{xi}	2.700(9)	**O(6)^{ix}-Li(4)-O(2)**	115.3(12)
Na(1)-O(2)^{viii}	2.700(9)	**O(3)^{ix}-Li(4)-O(2)**	102.4(9)
Na(1)-O(5)^{viii}	2.891(8)	**O(6)^{ix}-Li(4)-O(5)^{xi}**	108.0(9)
Na(1)-O(5)^{xi}	2.891(8)	**O(3)^{ix}-Li(4)-O(5)^{xi}**	120.9(12)
Li(1)-O(7)^{iv}	1.958(17)	**O(2)-Li(4)-O(5)^{xi}**	107.8(11)
Li(1)-O(12)^{xiv}	1.978(17)		
Li(1)-O(10)	1.971(19)		
Li(1)-O(12)^{viii}	2.00(2)		
Li(2)-O(11)^{iv}	1.957(19)		
Li(2)-O(10)	1.93(2)		
Li(2)-O(13)	1.771(17)		
Li(2)-O(11$^{)viii}$	2.01(2)		
Li(3)-O(4)^{i}	1.887(18)		
Li(3)-O(6)^{ii}	1.94(2)		
Li(3)-O(8)	1.93(3)		
Li(3)-O(9)^{vi}	1.971(18)		
Li(4)-O(6)^{ix}	1.90(2)		
Li(4)-O(3)^{ix}	1.925(18)		
Li(4)-O(5)^{xi}	2.01(3)		
Li(4)-O(2)	1.932(18)		

Symmetry codes: (i) -x+1,y+1,-z+2; (ii) x,y+1,z; (iii) -x+1,y,-z+2; (iv) -x+3/2,y-1/2,-z+3; (v)x,y,z+1; (vi) -x+3/2,y+1/2,-z+3; (vii) -x+1,y-1,-z+2; (viii) x,y-1,z; (ix) -x+1,y,-z+1; (x) x,y,z-1; (xi) -x+1,y-1,-z+1; (xii) -x+1,y+1,-z+1; (xiii) -x+3/2,y+1/2,-z+4; (xiv) -x+3/2,y-1/2,-z+4.