Electronic Supporting Information

Enhancing Birefringence of Non-π-Conjugated Sulfate Systems Through Rare-Earth Metal-Centered Polyhedra

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Table S1. Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$), and bond valence sum (BVS) calculations for $NaGd_2(SO_4)_2F_3$. *U*(eq) is defined as one–third of the trace of the orthogonalized U_{ij} tensor.

Atom	***x***	***y***	***z***	***U*(eq)**	**BVS**
Na(1)	5000	11198(3)	2500	18(1)	1.04
Gd(1)	6185(1)	5921(1)	4601(1)	8(1)	3.09
S(1)	6798(1)	884(1)	6604(1)	8(1)	6.09
O(1)	6947(2)	1520(3)	8466(3)	14(1)	2.02
O(2)	6196(2)	-893(3)	6083(3)	13(1)	2.02
O(3)	7778(2)	494(3)	6790(3)	15(1)	2.02
O(4)	6329(2)	2431(3)	5248(3)	14(1)	2.14
F(1)	5449(1)	5559(3)	6586(3)	14(1)	0.99
F(2)	5000	7819(4)	2500	15(1)	1.02

Table S2. Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$), and bond valence sum (BVS) calculations for $NaLa_2(SO_4)_2F_3$. *U*(eq) is defined as one–third of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	*U*(eq)	BVS
Na(1)	5000	3824(2)	7500	22(1)	0.89
La(1)	6204(1)	9086(1)	9630(1)	7(1)	3.26
S(1)	3214(1)	4138(1)	3385(1)	8(1)	6.03
O(1)	3061(1)	3498(2)	1572(2)	12(1)	2.03
O(2)	3683(1)	2644(2)	4717(2)	14(1)	2.06
O(3)	3798(1)	5866(2)	3871(3)	14(1)	1.99
O(4)	2264(1)	4528(3)	3219(2)	13(1)	2.04
F(1)	5000	7132(3)	7500	14(1)	1.06
F(2)	5454(1)	9419(2)	11606(2)	13(1)	1.08

Table S3. Anisotropic displacement parameters ($Å^2$) for $NaGd_2(SO_4)_2F_3$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Na(1)	18(1)	14(1)	19(1)	0	5(1)	0
Gd(1)	9(1)	7(1)	8(1)	0(1)	4(1)	0(1)
S(1)	10(1)	7(1)	7(1)	-1(1)	3(1)	0(1)
O(1)	20(1)	13(1)	8(1)	-2(1)	6(1)	-1(1)
O(2)	14(1)	10(1)	14(1)	-3(1)	5(1)	-4(1)
O(3)	12(1)	14(1)	21(1)	-4(1)	8(1)	0(1)
O(4)	18(1)	10(1)	12(1)	2(1)	3(1)	2(1)
F(1)	12(1)	17(1)	13(1)	1(1)	6(1)	-2(1)
F(2)	13(1)	9(1)	16(1)	0	0(1)	0

Table S4. Anisotropic displacement parameters (Å^2) for $NaLa_2(SO_4)_2F_3$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Na(1)	20(1)	17(1)	23(1)	0	6(1)	0
La(1)	7(1)	8(1)	7(1)	0(1)	3(1)	0(1)
S(1)	7(1)	8(1)	7(1)	0(1)	2(1)	0(1)
O(1)	14(1)	14(1)	9(1)	-2(1)	5(1)	1(1)
O(2)	17(1)	13(1)	9(1)	3(1)	2(1)	3(1)
O(3)	15(1)	11(1)	17(1)	-4(1)	8(1)	-5(1)
O(4)	8(1)	18(1)	14(1)	-3(1)	5(1)	1(1)
F(1)	11(1)	11(1)	15(1)	0	2(1)	0
F(2)	10(1)	18(1)	11(1)	-2(1)	5(1)	1(1)

Table S5. Selected bond lengths (Å) and angles (°) for $NaGd_2(SO_4)_2F_3$.

Selected bond lengths			
Gd(1) – F(1)$^{\#3}$	2.4120(19)	Na(1) – O(2)$^{\#3}$	2.550(2)
Gd(1) – F(1)	2.3302(19)	Na(1) – O(4)$^{\#5}$	2.427(2)
Gd(1) – F(1)$^{\#4}$	2.4810(19)	Na(1) – O(4)$^{\#8}$	2.427(2)
Gd(1) – F(2)	2.2767(15)	Na(1) – F(1)$^{\#10}$	2.502(2)
Gd(1) – O(1)$^{\#1}$	2.643(2)	Na(1) – F(1)$^{\#9}$	2.502(2)
Gd(1) – O(1)$^{\#3}$	2.471(2)	Na(1) – F(2)	2.284(3)
Gd(1) – O(2)$^{\#5}$	2.459(2)	S(1) – O(1)	1.479(2)
Gd(1) – O(3)$^{\#1}$	2.665(3)	S(1) – O(2)	1.463(2)
Gd(1) – O(3)$^{\#6}$	2.494(2)	S(1)–O(3)	1.471(3)
Gd(1) – O(4)	2.406(2)	S(1)–O(4)	1.459(2)
Na(1) – O(2)$^{\#4}$	2.550(2)		
Selected bond angles			
F(1)$^{\#3}$-Gd(1)-F(1)$^{\#4}$	58.94(8)	O(3)$^{\#6}$-Gd(1)-O(1)$^{\#1}$	65.39(8)
F(1)-Gd(1)-F(1)$^{\#3}$	119.34(7)	O(3)$^{\#6}$-Gd(1)-O(3)$^{\#1}$	104.42(8)
F(1)-Gd(1)-F(1)$^{\#4}$	60.98(8)	O(4)-Gd(1)-F(1)$^{\#4}$	70.86(7)
F(1)$^{\#4}$-Gd(1)-O(1)$^{\#1}$	162.13(7)	O(4)-Gd(1)-F(1)$^{\#3}$	76.78(7)
F(1)-Gd(1)-O(1)$^{\#3}$	140.48(7)	O(4)-Gd(1)-O(1)$^{\#1}$	92.69(8)
F(1)$^{\#3}$-Gd(1)-O(1)$^{\#3}$	90.62(7)	O(4)-Gd(1)-O(1)$^{\#3}$	138.80(8)
F(1)$^{\#3}$-Gd(1)-O(1)$^{\#1}$	125.41(7)	O(4)-Gd(1)-O(2)$^{\#5}$	140.64(8)
F(1)-Gd(1)-O(1)$^{\#1}$	109.51(7)	O(4)-Gd(1)-O(3)$^{\#1}$	72.60(8)
F(1)-Gd(1)-O(2)$^{\#5}$	70.39(7)	O(4)-Gd(1)-O(3)$^{\#6}$	72.79(8)
F(1)$^{\#3}$-Gd(1)-O(2)$^{\#5}$	138.95(7)	O(2)-S(1)-O(1)	109.60(14)
F(1)$^{\#3}$-Gd(1)-O(3)$^{\#6}$	60.29(7)	O(2)-S(1)-O(3)	111.99(14)
F(1)$^{\#4}$-Gd(1)-O(3)$^{\#6}$	114.01(7)	O(3)-S(1)-O(1)	103.88(14)
F(1)-Gd(1)-O(3)$^{\#1}$	58.68(7)	O(4)-S(1)-O(1)	111.25(14)
F(1)#3-Gd(1)-O(3)$^{\#1}$	148.88(7)	O(4)-S(1)-O(2)	108.98(14)
F(1)-Gd(1)-O(3)$^{\#6}$	148.93(7)	O(4)-S(1)-O(3)	111.10(15)
F(1)#4-Gd(1)-O(3)$^{\#1}$	114.22(7)	F(1)$^{\#9}$-Na(1)-F(1)$^{\#10}$	57.54(9)
F(1)-Gd(1)-O(4)	77.01(7)	F(1)$^{\#9}$-Na(1)-O(2)$^{\#4}$	66.29(7)
F(2)-Gd(1)-F(1)$^{\#3}$	66.73(6)	F(1)$^{\#9}$-Na(1)-O(2)$^{\#3}$	122.94(9)
F(2)-Gd(1)-F(1)	95.76(5)	F(1)$^{\#10}$-Na(1)-O(2)$^{\#4}$	122.94(9)

F(2)-Gd(1)-F(1)$^{\#4}$	65.55(6)	F(1)$^{\#10}$-Na(1)-O(2)$^{\#3}$	66.29(7)
F(2)-Gd(1)-O(1)$^{\#3}$	71.66(7)	F(2)-Na(1)-F(1)$^{\#10}$	151.23(5)
F(2)-Gd(1)-O(1)$^{\#1}$	132.20(7)	F(2)-Na(1)-F(1)$^{\#9}$	151.23(5)
F(2)-Gd(1)-O(2)$^{\#5}$	72.77(8)	F(2)-Na(1)-O(2)$^{\#3}$	85.37(6)
F(2)-Gd(1)-O(3)$^{\#1}$	141.78(6)	F(2)-Na(1)-O(2)$^{\#4}$	85.37(6)
F(2)-Gd(1)-O(3)$^{\#6}$	110.09(6)	F(2)-Na(1)-O(4)$^{\#5}$	110.09(7)
F(2)-Gd(1)-O(4)	133.13(8)	F(2)-Na(1)-O(4)$^{\#8}$	110.09(7)
O(1)$^{\#3}$-Gd(1)-F(1)$^{\#4}$	134.45(7)	O(2)$^{\#3}$-Na(1)-O(2)$^{\#4}$	170.73(13)
O(1)$^{\#3}$-Gd(1)-O(1)$^{\#1}$	62.92(9)	O(4)$^{\#5}$-Na(1)-F(1)$^{\#10}$	74.75(8)
O(1)$^{\#3}$-Gd(1)-O(3)$^{\#6}$	66.99(8)	O(4)$^{\#5}$-Na(1)-F(1)$^{\#9}$	70.18(8)
O(1)$^{\#3}$-Gd(1)-O(3)$^{\#1}$	108.79(8)	O(4)$^{\#8}$-Na(1)-F(1)$^{\#10}$	70.18(8)
O(1)$^{\#1}$-Gd(1)-O(3)$^{\#1}$	51.90(7)	O(4)$^{\#8}$-Na(1)-F(1)$^{\#9}$	74.75(8)
O(2)$^{\#5}$-Gd(1)-F(1)$^{\#4}$	109.63(7)	O(4)$^{\#5}$-Na(1)-O(2)$^{\#4}$	96.07(8)
O(2)$^{\#5}$-Gd(1)-O(1)$^{\#3}$	70.10(8)	O(4)$^{\#8}$-Na(1)-O(2)$^{\#4}$	87.12(8)
O(2)$^{\#5}$-Gd(1)-O(1)$^{\#1}$	78.42(8)	O(4)$^{\#8}$-Na(1)-O(2)$^{\#3}$	96.07(8)
O(2)$^{\#5}$-Gd(1)-O(3)$^{\#6}$	132.84(8)	O(4)$^{\#5}$-Na(1)-O(2)$^{\#3}$	87.12(8)
O(2)$^{\#5}$-Gd(1)-O(3)$^{\#1}$	71.90(8)	O(4)$^{\#5}$-Na(1)-O(4)$^{\#8}$	139.82(13)

Symmetry transformations used to generate equivalent atoms:

$^{\#1}$ – x + 3/2, y + 1/2, – z + 3/2 $^{\#2}$ x, y – 1, z $^{\#3}$ x, – y + 1, z – 1/2
$^{\#4}$ – x + 1, – y + 1, – z + 1 $^{\#5}$ x, y + 1, z $^{\#6}$ – x + 3/2, – y + 1/2, –z + 1
$^{\#7}$ – x + 3/2, y – 1/2, – z + 3/2 $^{\#8}$ – x + 1, y + 1, – z + 1/2 $^{\#9}$ – x + 1, – y + 2, – z + 1
$^{\#10}$ x, – y + 2, z – 1/2 $^{\#11}$ x, – y + 1, z + 1/2 $^{\#12}$ – x + 1, y, – z + 1/2

Table S6. Selected bond lengths (Å) and angles (°) for $NaLa_2(SO_4)_2F_3$.

Selected bond lengths			
La(1)-F(1)	2.3838(11)	Na(1)-O(2)	2.4836(19)
La(1)-F(2)$^{\#3}$	2.4921(14)	Na(1)-O(3)$^{\#14}$	2.612(2)
La(1)-F(2)	2.4155(14)	Na(1)-O(3)$^{\#5}$	2.612(2)
La(1)-F(2)$^{\#4}$	2.5801(15)	Na(1)-F(1)	2.311(2)
La(1)-O(1)$^{\#1}$	2.6951(17)	Na(1)-F(2)$^{\#12}$	2.5801(19)
La(1)-O(1)$^{\#5}$	2.5702(16)	Na(1)-F(2)$^{\#13}$	2.5801(19)
La(1)-O(2)$^{\#6}$	2.5334(16)	S(1)-O(1)	1.4862(17)
La(1)-O(3)$^{\#7}$	2.5710(16)	S(1)-O(2)	1.4661(17)
La(1)-O(4)$^{\#1}$	2.7282(18)	S(1)-O(3)	1.4650(16)
La(1)-O(4)$^{\#8}$	2.6101(18)	S(1)-O(4)	1.4716(18)
Na(1)-O(2)$^{\#7}$	2.4836(19)		
Selected bond angles			
F(1)-La(1)-F(2)$^{\#4}$	65.96(4)	O(2)$^{\#6}$-La(1)-O(3)$^{\#7}$	140.31(6)
F(1)-La(1)-F(2)	95.21(4)	O(2)$^{\#6}$-La(1)-O(4)$^{\#1}$	72.69(6)
F(1)-La(1)-F(2)$^{\#3}$	67.40(5)	O(2)$^{\#6}$-La(1)-O(4)$^{\#8}$	74.51(6)
F(1)-La(1)-O(1)$^{\#5}$	70.07(5)	O(3)$^{\#7}$-La(1)-F(2)$^{\#4}$	109.44(6)
F(1)-La(1)-O(1)$^{\#1}$	131.78(5)	O(3)$^{\#7}$-La(1)-O(1)$^{\#1}$	78.83(6)
F(1)-La(1)-O(2)$^{\#6}$	132.83(6)	O(3)$^{\#7}$-La(1)-O(4)$^{\#1}$	72.52(6)
F(1)-La(1)-O(3)$^{\#7}$	71.95(6)	O(3)$^{\#7}$-La(1)-O(4)$^{\#8}$	132.61(6)
F(1)-La(1)-O(4)$^{\#8}$	109.85(4)	O(4)$^{\#8}$-La(1)-O(1)$^{\#1}$	65.27(5)
F(1)-La(1)-O(4)$^{\#1}$	142.03(5)	O(4)$^{\#8}$-La(1)-O(4)$^{\#1}$	103.82(6)
F(2)-La(1)-F(2)$^{\#3}$	119.01(5)	O(2)-S(1)-O(1)	110.88(10)
F(2)-La(1)-F(2)$^{\#4}$	61.30(6)	O(2)-S(1)-O(4)	111.31(11)
F(2)$^{\#3}$-La(1)-F(2)$^{\#4}$	58.23(6)	O(3)-S(1)-O(1)	109.48(11)
F(2)$^{\#4}$-La(1)-O(1)$^{\#1}$	162.15(5)	O(3)-S(1)-O(2)	109.15(11)
F(2)-La(1)-O(1)$^{\#1}$	109.60(5)	O(3)-S(1)-O(4)	111.51(11)
F(2)$^{\#3}$-La(1)-O(1)$^{\#5}$	90.04(5)	O(4)-S(1)-O(1)	104.44(10)
F(2)$^{\#3}$-La(1)-O(1)$^{\#1}$	125.75(5)	F(1)-Na(1)-F(2)$^{\#13}$	151.41(3)
F(2)-La(1)-O(1)$^{\#5}$	140.21(5)	F(1)-Na(1)-F(2)$^{\#12}$	151.41(3)
F(2)-La(1)-O(2)$^{\#6}$	76.70(5)	F(1)-Na(1)-O(2)$^{\#7}$	109.39(5)
F(2)$^{\#3}$-La(1)-O(2)$^{\#6}$	76.29(5)	F(1)-Na(1)-O(2)	109.39(5)

F(2)-La(1)-O(3)$^{\#7}$	69.63(5)	F(1)-Na(1)-O(3)$^{\#5}$	85.25(5)
F(2)$^{\#3}$-La(1)-O(3)$^{\#7}$	138.95(6)	F(1)-Na(1)-O(3)$^{\#14}$	85.25(4)
F(2)-La(1)-O(4)$^{\#8}$	150.23(5)	F(2)$^{\#12}$-Na(1)-F(2)$^{\#13}$	57.17(7)
F(2)$^{\#4}$-La(1)-O(4)$^{\#1}$	115.09(5)	F(2)$^{\#13}$-Na(1)-O(3)$^{\#14}$	66.58(5)
F(2)$^{\#3}$-La(1)-O(4)$^{\#8}$	60.64(5)	F(2)$^{\#12}$-Na(1)-O(3)$^{\#14}$	122.88(6)
F(2)$^{\#4}$-La(1)-O(4)$^{\#8}$	114.12(5)	F(2)$^{\#12}$-Na(1)-O(3)$^{\#5}$	66.58(5)
F(2)-La(1)-O(4)$^{\#1}$	59.79(5)	F(2)$^{\#13}$-Na(1)-O(3)$^{\#5}$	122.88(6)
F(2)$^{\#3}$-La(1)-O(4)$^{\#1}$	148.24(5)	O(2)-Na(1)-F(2)$^{\#13}$	75.59(6)
O(1)$^{\#5}$-La(1)-F(2)$^{\#4}$	132.91(5)	O(2)$^{\#7}$-Na(1)-F(2)$^{\#12}$	75.59(6)
O(1)$^{\#5}$-La(1)-O(1)$^{\#1}$	64.36(6)	O(2)$^{\#7}$-Na(1)-F(2)$^{\#13}$	70.48(6)
O(1)$^{\#5}$-La(1)-O(3)$^{\#7}$	70.65(6)	O(2)-Na(1)-F(2)$^{\#12}$	70.48(6)
O(1)$^{\#1}$-La(1)-O(4)$^{\#1}$	51.07(5)	O(2)$^{\#7}$-Na(1)-O(2)	141.22(10)
O(1)$^{\#5}$-La(1)-O(4)$^{\#8}$	66.46(5)	O(2)$^{\#7}$-Na(1)-O(3)$^{\#5}$	87.68(6)
O(1)$^{\#5}$-La(1)-O(4)$^{\#1}$	109.68(5)	O(2)$^{\#7}$-Na(1)-O(3)$^{\#14}$	95.48(6)
O(2)$^{\#6}$-La(1)-F(2)$^{\#4}$	69.71(5)	O(2)-Na(1)-O(3)$^{\#14}$	87.68(6)
O(2)$^{\#6}$-La(1)-O(1)$^{\#5}$	140.37(6)	O(2)-Na(1)-O(3)$^{\#5}$	95.48(6)
O(2)$^{\#6}$-La(1)-O(1)$^{\#1}$	93.69(6)	O(3)$^{\#5}$-Na(1)-O(3)$^{\#14}$	170.49(9)

Symmetry transformations used to generate equivalent atoms:

$^{\#1}$ x + 1/2, y + 1/2, z + 1
$^{\#2}$ x, y + 1, z
$^{\#3}$ x, – y + 2, z – 1/2
$^{\#4}$ – x + 1, – y + 2, – z + 2
$^{\#5}$ – x + 1, – y + 1, – z + 1
$^{\#6}$ – x + 1, y + 1, – z + 3/2
$^{\#7}$ – x + 1, y, – z + 3/2
$^{\#8}$ x + 1/2, – y + 3/2, z + 1/2
$^{\#9}$ x – 1/2, y – 1/2, z – 1
$^{\#10}$ x, y – 1, z
$^{\#11}$ – x + 1, y – 1, – z + 3/2
$^{\#12}$ x, – y + 1, z – 1/2
$^{\#13}$ – x + 1, – y + 1, – z + 2
$^{\#14}$ x, – y + 1, z + 1/2
$^{\#15}$ x, – y + 2, z + 1/2
$^{\#16}$ x – 1/2, – y + 3/2, z – 1/2

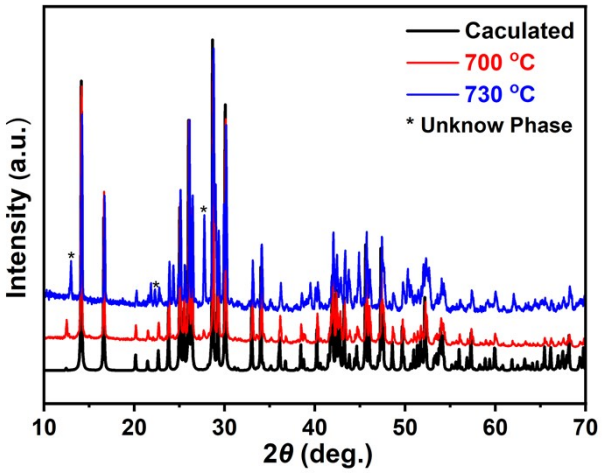

Figure S1. Calculated powder XRD pattern of $NaLa_2(SO_4)_2F_3$ and the powder XRD patterns after heating at 700 and 730 °C, respectively.

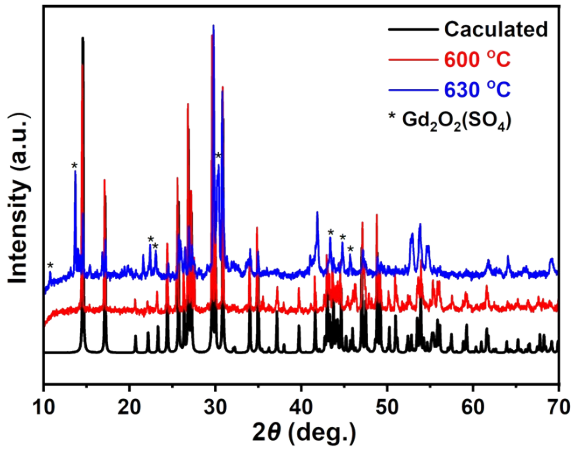

Figure S2. Calculated powder XRD pattern of $NaGd_2(SO_4)_2F_3$ and the powder XRD patterns after heating at 600 and 630 °C, respectively.