$NaCaGa_3S_6$: A Mixed Alkali Metal and Alkaline Earth Metal Sulfide with a Distinctive $[Ga_5S_{10}]_\infty$ Layered Framework

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Figure S1. The crystals of NCGS.

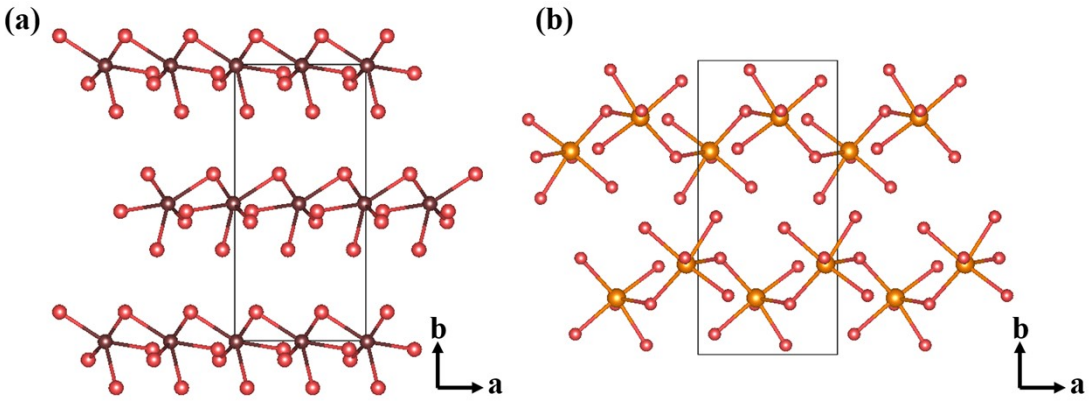

Figure S2. (a) one-dimensional (1D) $[Na_2S_8]_\infty$ chains and (b) 1D $[Ca_2S_{10}]_\infty$ chains.

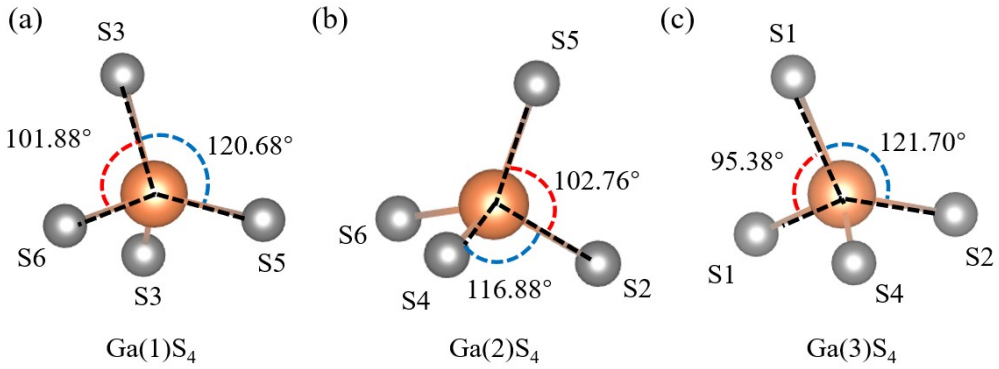

Figure S3. The bond-angle difference of GaS_4 groups in NCGS.

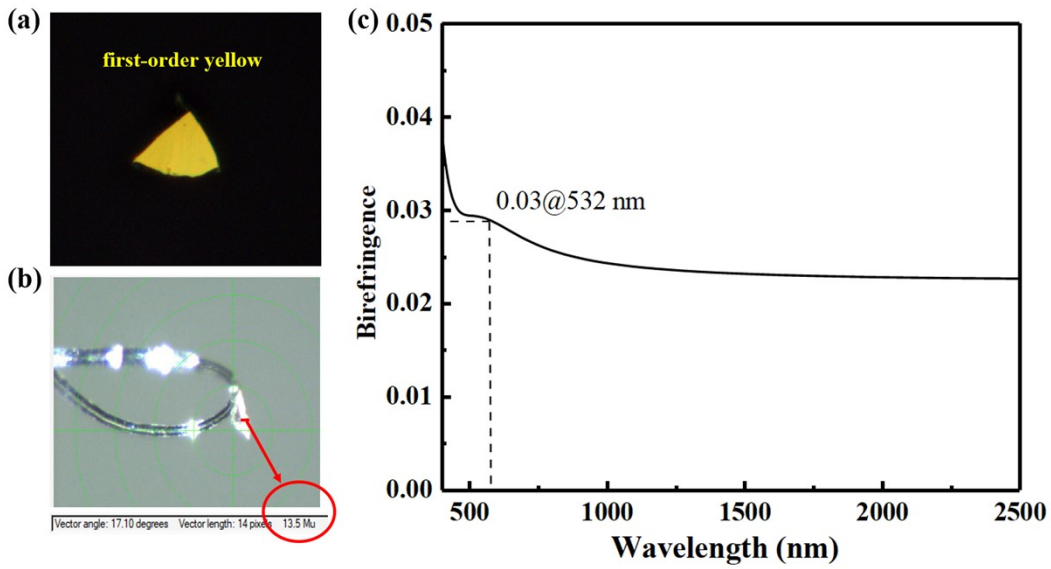

Figure S4. (a) The interference color of NCGS observed in the cross-polarized light, (b) The thickness of NCGS crystal, (c) The calculated birefringence curve for NCGS.

Table S1. Crystal data and structure refinement for NCGS

Empirical formula	$NaCaGa_3S_6$
Formula weight	206.48
Temperature (K)	297(2)
Crystal system	Orthorhombic
Space group	*Pbca*
Z	18
a (Å)	6.9613(5)
b (Å)	14.6439(9)
c (Å)	20.1221(15)
V (Å^3)	2051.3(2)
D_c (g cm^{-3})	3.009
μ (mm^{-1})	9.515
F(000)	1760
Radiation	Mo-K_α (λ = 0.71073)
2θ range(°)	2.024 to 27.502
Reflections collected	17376
Indep. Reflns/ Rint	2350/0.0398
GOOF on F^2	1.142
R_1, wR_2 (I >2σ(I))[a]	0.0212, 0.0387
R_1, wR_2 (all data)	0.0278, 0.0468
largest diff. peak and hole (e·Å^{-3})	0.511, -0.699

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, [b] $wR_2 = \Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S2. Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$) and bond valence sums (BVS) for NCGS. Ueq is defined as one-third of the trace of the orthogonalized U*ij* tensor.

Atom	BVS[a]	x	y	z	U_{eq}(Å)
Na(1)	1.146	4895(2)	4966(1)	1845(1)	33(1)
Ca(1)	1.911	10847(1)	8076(1)	4170(1)	18(1)
Ga(1)	2.904	8286(1)	7375(1)	2670(1)	12(1)
Ga(2)	2.972	5204(1)	6130(1)	3810(1)	12(1)
Ga(3)	2.909	8097(1)	4503(1)	4856(1)	13(1)
S(1)	1.830	8813(1)	5694(1)	5532(1)	15(1)
S(2)	1.897	6289(1)	4684(1)	3933(1)	16(1)
S(3)	1.813	5941(1)	8294(1)	2275(1)	16(1)
S(4)	1.858	6590(1)	3279(1)	5333(1)	14(1)
S(5)	1.938	3376(1)	6035(1)	2894(1)	16(1)
S(6)	2.030	7842(2)	7004(1)	3748(1)	31(1)

[a]Bond valence state was calculated using the empirical formula $V_i=\Sigma S_{ij}=\Sigma\exp[(r_0-r_{ij})/0.37]$, where S_{ij} is the bond valence associated with bond lengths r_{ij} and r_0.

Table S3. Selected bond distances (Å) and angles (°).

Na(1)-S(5)	2.8326(18)	Ga(2)-S(5)	2.2452(9)
Na(1)-S(5)#1	2.9327(18)	Ga(2)-S(2)	2.2626(9)
Na(1)-S(1)#2	2.9540(18)	Ga(2)-S(4)#8	2.2971(9)
Na(1)-S(2)#3	2.9871(19)	Ga(3)-S(2)	2.2593(9)
Na(1)-S(3)#4	3.078(2)	Ga(3)-S(1)	2.2663(9)
Ca(1)-S(6)	2.7498(12)	Ga(3)-S(4)	2.2869(9)
Ca(1)-S(1)#5	2.8050(11)	Ga(3)-S(1)#7	2.3069(9)
Ca(1)-S(2)#6	2.8253(11)	Ga(2)-S(5)	2.2452(9)
Ca(1)-S(4)#7	2.8498(11)	Ga(2)-S(2)	2.2626(9)
Ca(1)-S(4)#6	2.9051(12)	Ga(2)-S(4)#8	2.2971(9)
Ca(1)-S(3)#1	2.9267(12)	Ga(3)-S(2)	2.2593(9)
Ca(1)-Ga(1)	3.6530(8)	Ga(3)-S(1)	2.2663(9)
Ca(1)-Ga(3)#6	3.7161(8)	Ga(3)-S(4)	2.2869(9)
Ga(1)-S(6)	2.2578(10)	Ga(3)-S(1)#7	2.3069(9)
Ga(1)-S(3)	2.2596(9)	Ga(2)-S(5)	2.2452(9)
Ga(1)-S(5)#1	2.2673(9)	Ga(2)-S(2)	2.2626(9)
Ga(1)-S(3)#1	2.2889(9)	Ga(2)-S(4)#8	2.2971(9)
Ga(2)-S(6)	2.2417(10)	Ga(3)-S(2)	2.2593(9)
Ga(2)-S(5)	2.2452(9)	S(5)-Na(1)-S(5)#1	83.09(5)
Ga(2)-S(2)	2.2626(9)	S(5)-Na(1)-S(1)#2	163.94(8)
Ga(2)-S(4)#8	2.2971(9)	S(5)#1-Na(1)-S(1)#2	94.77(5)
Ga(3)-S(2)	2.2593(9)	S(5)-Na(1)-S(2)#3	98.83(6)
Ga(3)-S(1)	2.2663(9)	S(5)#1-Na(1)-S(2)#3	149.56(7)
Ga(3)-S(4)	2.2869(9)	S(1)#2-Na(1)-S(2)#3	75.03(4)
Ga(3)-S(1)#7	2.3069(9)	S(5)-Na(1)-S(3)#4	86.60(5)
Na(1)-S(5)	2.8326(18)	S(5)#1-Na(1)-S(3)#4	118.56(6)
Na(1)-S(5)#1	2.9327(18)	S(1)#2-Na(1)-S(3)#4	108.18(6)
Na(1)-S(1)#2	2.9540(18)	S(2)#3-Na(1)-S(3)#4	91.86(5)
Na(1)-S(2)#3	2.9871(19)	S(6)-Ca(1)-S(1)#5	173.03(4)
Na(1)-S(3)#4	3.078(2)	S(6)-Ca(1)-S(2)#6	91.32(4)
Ca(1)-S(6)	2.7498(12)	S(1)#5-Ca(1)-S(2)#6	83.58(3)
Ca(1)-S(1)#5	2.8050(11)	S(6)-Ca(1)-S(4)#7	100.79(4)
Ca(1)-S(2)#6	2.8253(11)	S(1)#5-Ca(1)-S(4)#7	84.93(3)
Ca(1)-S(4)#7	2.8498(11)	S(2)#6-Ca(1)-S(4)#7	165.73(4)
Ca(1)-S(4)#6	2.9051(12)	S(6)-Ca(1)-S(4)#6	82.12(3)
Ca(1)-S(3)#1	2.9267(12)	S(1)#5-Ca(1)-S(4)#6	101.05(3)
Ca(1)-Ga(1)	3.6530(8)	S(2)#6-Ca(1)-S(4)#6	75.12(3)
Ca(1)-Ga(3)#6	3.7161(8)	S(4)#7-Ca(1)-S(4)#6	98.90(3)
Ga(1)-S(6)	2.2578(10)	S(6)-Ca(1)-S(3)#1	76.84(3)
Ga(1)-S(3)	2.2596(9)	S(1)#5-Ca(1)-S(3)#1	97.23(3)
Ga(1)-S(3)#1	2.2889(9)	S(4)#7-Ca(1)-S(3)#1	114.22(3)
Ga(2)-S(6)	2.2417(10)	S(4)#6-Ca(1)-S(3)#1	143.34(4)
S(6)-Ca(1)-Ga(1)	38.11(2)	S(2)-Ga(3)-Ca(1)#9	49.38(2)

S(1)#5-Ca(1)-Ga(1)	135.75(3)	S(1)-Ga(3)-Ca(1)#9	144.87(3)
S(2)#6-Ca(1)-Ga(1)	80.65(3)	S(4)-Ga(3)-Ca(1)#9	51.42(3)
S(4)#7-Ca(1)-Ga(1)	113.56(3)	S(1)#7-Ga(3)-Ca(1)#9	119.55(3)
S(4)#6-Ca(1)-Ga(1)	114.16(3)	Ga(3)-S(1)-Ga(3)#7	84.62(3)
S(3)#1-Ca(1)-Ga(1)	38.77(2)	Ga(3)-S(1)-Ca(1)#10	117.43(4)
S(6)-Ca(1)-Ga(3)#6	82.73(3)	Ga(3)#7-S(1)-Ca(1)#10	147.01(4)
S(1)#5-Ca(1)-Ga(3)#6	95.92(3)	Ga(3)-S(1)-Na(1)#11	110.60(5)
S(2)#6-Ca(1)-Ga(3)#6	37.37(2)	Ga(3)#7-S(1)-Na(1)#11	88.74(4)
S(4)#7-Ca(1)-Ga(3)#6	136.38(3)	Ca(1)#10-S(1)-Na(1)#11	104.07(5)
S(4)#6-Ca(1)-Ga(3)#6	37.980(19)	Ga(3)-S(2)-Ga(2)	112.66(4)
S(3)#1-Ca(1)-Ga(3)#6	108.93(3)	Ga(3)-S(2)-Ca(1)#9	93.24(3)
Ga(1)-Ca(1)-Ga(3)#6	95.989(19)	Ga(2)-S(2)-Ca(1)#9	128.53(4)
S(6)-Ga(1)-S(3)	112.49(4)	Ga(3)-S(2)-Na(1)#1	88.82(4)
S(6)-Ga(1)-S(5)#1	106.06(4)	Ga(2)-S(2)-Na(1)#1	95.38(4)
S(3)-Ga(1)-S(5)#1	111.03(4)	Ca(1)#9-S(2)-Na(1)#1	130.26(5)
S(6)-Ga(1)-S(3)#1	101.88(4)	Ga(1)-S(3)-Ga(1)#3	102.51(3)
S(3)-Ga(1)-S(3)#1	104.50(4)	Ga(1)-S(3)-Ca(1)#3	107.52(4)
S(5)#1-Ga(1)-S(3)#1	120.68(4)	Ga(1)#3-S(3)-Ca(1)#3	88.03(3)
S(6)-Ga(1)-Ca(1)	48.73(3)	Ga(1)-S(3)-Na(1)#12	114.07(5)
S(3)-Ga(1)-Ca(1)	118.43(3)	Ga(1)#3-S(3)-Na(1)#12	106.70(5)
S(5)#1-Ga(1)-Ca(1)	130.04(3)	Ca(1)#3-S(3)-Na(1)#12	130.85(4)
S(3)#1-Ga(1)-Ca(1)	53.20(3)	Ga(3)-S(4)-Ga(2)#8	105.62(3)
S(6)-Ga(2)-S(5)	116.99(4)	Ga(3)-S(4)-Ca(1)#7	113.92(4)
S(6)-Ga(2)-S(2)	105.49(4)	Ga(2)#8-S(4)-Ca(1)#7	109.83(4)
S(5)-Ga(2)-S(2)	102.76(3)	Ga(3)-S(4)-Ca(1)#9	90.60(3)
S(6)-Ga(2)-S(4)#8	105.79(4)	Ga(2)#8-S(4)-Ca(1)#9	108.99(4)
S(5)-Ga(2)-S(4)#8	109.36(4)	Ca(1)#7-S(4)-Ca(1)#9	125.21(3)
S(2)-Ga(2)-S(4)#8	116.87(3)	Ga(2)-S(5)-Ga(1)#3	111.93(4)
S(2)-Ga(3)-S(1)	121.70(3)	Ga(2)-S(5)-Na(1)	115.76(5)
S(2)-Ga(3)-S(4)	100.44(3)	Ga(1)#3-S(5)-Na(1)	96.64(5)
S(1)-Ga(3)-S(4)	116.88(3)	Ga(2)-S(5)-Na(1)#3	110.75(5)
S(2)-Ga(3)-S(1)#7	104.81(4)	Ga(1)#3-S(5)-Na(1)#3	121.93(5)
S(1)-Ga(3)-S(1)#7	95.38(3)	Na(1)-S(5)-Na(1)#3	98.44(6)
S(4)-Ga(3)-S(1)#7	118.18(3)	Ga(2)-S(6)-Ga(1)	107.64(4)
Ga(1)-S(6)-Ca(1)	93.16(4)	Ga(2)-S(6)-Ca(1)	158.73(5)

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,y,-z+1/2 #2 -x+3/2,-y+1,z-1/2 #3 x-1/2,y,-z+1/2

#4 -x+1,y-1/2,-z+1/2 #5 x+1/2,-y+3/2,-z+1 #6 -x+3/2,y+1/2,z

#7 -x+2,-y+1,-z+1 #8 -x+1,-y+1,-z+1 #9 -x+3/2,y-1/2,z

#10 x-1/2,-y+3/2,-z+1 #11 -x+3/2,-y+1,z+1/2

#12 -x+1,y+1/2,-z+1/2