Supporting Information

$Na_4Ga_8S_{14}$: A Ga-riched wide band gap ternary alkali-metal sulfide with unique [$Ga_{12}S_{42}$] 12-menbered rings

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Table S1. Crystal data and structure refinement for $Na_4Ga_8S_{14}$.

Empirical formula	$Na_4Ga_8S_{14}$
Formula weight ($g \cdot mol^{-1}$)	549.28
Crystal system	Orthorhombic
Space group	*Pbca*
a (Å)	13.5260(4)
b (Å)	11.4979(3)
c (Å)	29.9592(9)
α (deg)	90
V ($Å^3$)	4659.3(2)
Z	8
D_c ($g.cm^{-3}$)	3.132
μ (mm^{-1})	10.424
F(000)	4128
Data/restraints/parameters	5331/0/236
GOF on F^2	1.068
R_1, wR_2 ($I > 2\sigma(I)$)[a]	0.0297, 0.0521
R_1, wR_2 (all data)[a]	0.0404, 0.0556
Largest diff peak/hole, $e \cdot Å^{-3}$	0.67/-0.76

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

Table S2. Atomic coordinates, equivalent isotropic displacement parameters and bond valence calculation for $Na_4Ga_8S_{14}$.

Atom	Wyckoff	X	Y	Z	Ueq	BVS
Na1	8c	-364(1)	2292(2)	4448(1)	31(1)	1.2
Na2	8c	3712(2)	9360(2)	5489(1)	49(1)	0.79
Na3	8c	5683(1)	8150(2)	6963(1)	36(1)	1
Na4	8c	5934(1)	4269(2)	6924(1)	35(1)	1.22
Ga1	8c	5819(1)	6356(1)	5826(1)	13(1)	2.97
Ga2	8c	3563(1)	5545(1)	6377(1)	13(1)	2.97
Ga3	8c	3584(1)	5976(1)	5258(1)	15(1)	2.89
Ga4	8c	2188(1)	6123(1)	4447(1)	14(1)	2.97
Ga5	8c	1484(1)	3789(1)	3750(1)	14(1)	2.85
Ga6	8c	2206(1)	4046(1)	2537(1)	14(1)	2.88
Ga7	8c	1975(1)	1613(1)	1839(1)	13(1)	2.93
Ga8	8c	4008(1)	3800(1)	1695(1)	13(1)	2.91
S1	8c	6209(1)	4576(1)	5512(1)	15(1)	1.98
S2	8c	5108(1)	6128(1)	6490(1)	16(1)	2.24
S3	8c	2402(1)	7015(1)	6350(1)	13(1)	1.92
S4	8c	3367(1)	4519(1)	5743(1)	18(1)	2.08
S5	8c	4810(1)	7283(1)	5350(1)	16(1)	2.06
S6	8c	2130(1)	6882(1)	5135(1)	23(1)	1.88
S7	8c	1046(1)	4731(1)	4379(1)	18(1)	1.72
S8	8c	2126(1)	7548(1)	3905(1)	14(1)	1.91
S9	8c	211(1)	2611(1)	3575(1)	14(1)	2.07
S10	8c	2024(1)	4977(1)	3201(1)	16(1)	1.92
S11	8c	3837(1)	3766(1)	2440(1)	17(1)	1.95
S12	8c	1284(1)	2439(1)	2439(1)	17(1)	2
S13	8c	3340(1)	508(1)	2028(1)	13(1)	1.87
S14	8c	4161(1)	5630(1)	1437(1)	17(1)	1.93

Table S3. Selected bond lengths [Å] for $Na_4Ga_8S_{14}$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Na1	S7	3.399(2)	Ga2	S13[2]	2.3156(10)
Na1	S9	2.7553(19)	Ga2	S2	2.2198(11)
Na1[11]	S1	3.025(2)	Ga2	S3	2.3089(11)
Na1[11]	S4	2.758(2)	Ga2	S4	2.2532(10)
Na1[13]	S6	2.857(2)	Ga3	S1[7]	2.4089(10)
Na1[6]	S5	2.8035(19)	Ga3	S4	2.2359(11)
Na2	S5	2.843(2)	Ga3	S5	2.2552(11)
Na2[12]	S14	2.904(2)	Ga3	S6	2.2548(11)
Na2[3]	S4	2.920(2)	Ga4	S1[7]	2.3160(11)
Na2[3]	S6	3.291(2)	Ga4	S6	2.2394(11)
Na2[3]	S7	3.370(2)	Ga4	S7	2.2326(11)
Na2[8]	S7	3.348(3)	Ga4	S8	2.3102(10)
Na3	S2	2.831(2)	Ga5	S10	2.2603(10)
Na3[12]	S14	2.947(2)	Ga5	S7	2.2527(10)
Na3[4]	S12	3.094(2)	Ga5	S8[3]	2.4049(10)
Na3[7]	S11	2.911(2)	Ga5	S9	2.2526(11)
Na3[8]	S8	3.348(2)	Ga6	S10	2.2707(10)
Na3[8]	S10	2.857(2)	Ga6	S11	2.2489(11)
Na4	S2	2.740(2)	Ga6	S12	2.2478(11)
Na4[10]	S9	2.804(2)	Ga6	S13[6]	2.3863(10)
Na4[10]	S12	2.779(2)	Ga7	S12	2.2369(10)
Na4[7]	S10	2.920(2)	Ga7	S13	2.3123(10)
Na4[7]	S11	2.972(2)	Ga7	S14[3]	2.2547(11)
Na4[9]	S13	3.532(2)	Ga7	S3[4]	2.3120(10)
Ga1	S1	2.3149(11)	Ga8	S11	2.2436(10)
Ga1	S2	2.2248(10)	Ga8	S14	2.2515(11)
Ga1	S5	2.2440(10)	Ga8	S3[4]	2.3626(10)
Ga1	S8[1]	2.3159(10)	Ga8	S9[5]	2.2738(10)

[1]x+1/2,-y+3/2,-z+1; [2]x,-y+1/2,z+1/2; [3]-x+1/2,y-1/2,z; [4]-x+1/2,-y+1,z-1/2;

[5]x+1/2,y,-z+1/2; [6]-x+1/2,y+1/2,z;[7]-x+1,-y+1,-z+1; [8]x-1/2,-y+3/2,-z+1;

[9]x,-y+1/2,z-1/2; [10]x-1/2,-y+1/2,-z+1;[11]x+1/2,-y+1/2,-z+1; [12]x,-y+3/2,z-1/2;

[13]-x,-y+1,-z+1; [14]-x+1,y+1/2,-z+3/2;[15] -x+1/2,-y+1,z+1/2; [16] x-1/2,y,-z+1/2;

[17] x,-y+3/2,z+1/2; [18] -x+1,y-1/2,-z+3/2

Table S4 Selected angles [°] for $Na_4Ga_8S_{14}$.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
S1	Ga1	$S8^{1}$	116.66(4)	$S5^{3}$	Na1	$S1^{10}$	76.76(5)
S5	Ga1	$S8^{1}$	115.29(4)	$S5^{3}$	Na1	S7	84.95(5)
S5	Ga1	S1	107.41(4)	$S5^{3}$	Na1	$S6^{13}$	78.70(5)
S2	Ga1	$S8^{1}$	94.77(4)	$S4^{10}$	Na1	$S1^{10}$	84.83(6)
S2	Ga1	S1	111.01(4)	$S4^{10}$	Na1	$S5^{3}$	111.32(7)
S2	Ga1	S5	111.23(4)	$S4^{10}$	Na1	S7	163.65(7)
S3	Ga2	$S13^{2}$	108.91(4)	$S4^{10}$	Na1	$S6^{13}$	79.73(6)
S4	Ga2	S3	105.83(4)	$S6^{13}$	Na1	$S1^{10}$	143.77(7)
S4	Ga2	$S13^{2}$	114.94(4)	$S6^{13}$	Na1	S7	102.81(6)
S2	Ga2	S3	115.11(4)	$S10^{1}$	Na3	$S8^{1}$	71.21(5)
S2	Ga2	$S13^{2}$	98.76(4)	$S10^{1}$	Na3	$S14^{17}$	89.61(6)
S2	Ga2	S4	113.44(4)	$S10^{1}$	Na3	$S12^{15}$	142.16(8)
S9	Ga5	$S8^{3}$	106.62(4)	$S10^{1}$	Na3	$S11^{7}$	122.28(7)
S9	Ga5	S10	116.13(4)	$S14^{17}$	Na3	$S8^{1}$	96.11(6)
S9	Ga5	S7	106.45(4)	$S14^{17}$	Na3	$S12^{15}$	75.48(5)
S10	Ga5	$S8^{3}$	104.28(4)	$S12^{15}$	Na3	$S8^{1}$	143.76(7)
S7	Ga5	$S8^{3}$	109.24(4)	S2	Na3	$S8^{1}$	64.87(5)
S7	Ga5	S10	113.77(4)	S2	Na3	$S10^{1}$	135.05(8)
$S9^{5}$	Ga8	$S3^{4}$	100.61(4)	S2	Na3	$S14^{17}$	86.06(6)
S14	Ga8	$S3^{4}$	107.14(4)	S2	Na3	$S12^{15}$	79.28(5)
S14	Ga8	$S9^{5}$	111.97(4)	S2	Na3	$S11^{7}$	75.37(5)
S11	Ga8	$S3^{4}$	110.21(4)	$S11^{7}$	Na3	$S8^{1}$	99.55(6)
S11	Ga8	$S9^{5}$	114.60(4)	$S11^{7}$	Na3	$S14^{17}$	147.58(7)
S11	Ga8	S14	111.53(4)	$S11^{7}$	Na3	$S12^{15}$	75.11(5)
$S3^{4}$	Ga7	S13	103.86(4)	$S9^{11}$	Na4	$S13^{2}$	75.92(5)
$S14^{3}$	Ga7	$S3^{4}$	104.61(4)	$S9^{11}$	Na4	$S10^{7}$	119.39(8)
$S14^{3}$	Ga7	S13	113.57(4)	$S9^{11}$	Na4	$S11^{7}$	164.63(8)
S12	Ga7	$S3^{4}$	111.82(4)	$S10^{7}$	Na4	$S13^{2}$	158.41(7)
S12	Ga7	S13	111.66(4)	$S10^{7}$	Na4	$S11^{7}$	75.97(5)
S12	Ga7	$S14^{3}$	110.92(4)	$S12^{11}$	Na4	$S13^{2}$	99.21(6)
S10	Ga6	$S13^{6}$	101.13(4)	$S12^{11}$	Na4	$S9^{11}$	83.15(6)
S12	Ga6	$S13^{6}$	108.89(4)	$S12^{11}$	Na4	$S10^{7}$	97.83(6)
S12	Ga6	S10	116.26(4)	$S12^{11}$	Na4	$S11^{7}$	94.54(6)
S12	Ga6	S11	114.15(4)	S2	Na4	$S13^{2}$	65.18(5)
S11	Ga6	$S13^{6}$	108.75(4)	S2	Na4	$S9^{11}$	101.92(6)
S11	Ga6	S10	106.71(4)	S2	Na4	$S10^{7}$	95.37(6)

S5	Ga3	S1[7]	101.89(4)	S2	Na4	S12[11]	161.18(9)
S4	Ga3	S1[7]	116.10(4)	S2	Na4	S11[7]	75.72(5)
S4	Ga3	S5	121.09(4)	S11[7]	Na4	S13[2]	89.52(6)
S4	Ga3	S6	109.77(4)	S14[17]	Na2	S4[6]	86.93(6)
S6	Ga3	S1[7]	93.83(4)	S14[17]	Na2	S7[1]	71.73(6)
S6	Ga3	S5	110.69(4)	S14[17]	Na2	S7[6]	160.87(9)
S8	Ga4	S1[7]	108.47(4)	S14[17]	Na2	S6[6]	112.60(7)
S7	Ga4	S8	114.75(4)	S5	Na2	S14[17]	92.16(6)
S7	Ga4	S1[7]	113.84(4)	S5	Na2	S4[6]	126.42(9)
S7	Ga4	S6	109.88(4)	S5	Na2	S7[6]	84.89(6)
S6	Ga4	S8	111.71(4)	S5	Na2	S7[1]	77.71(6)
S6	Ga4	S1[7]	96.83(4)	S5	Na2	S6[6]	150.89(8)
S9	Na1	S1[10]	86.18(5)	S4[6]	Na2	S7[6]	110.02(7)
S9	Na1	S5[3]	147.16(8)	S4[6]	Na2	S7[1]	149.11(8)
S9	Na1	S4[10]	94.54(6)	S4[6]	Na2	S6[6]	72.25(5)
S9	Na1	S7	70.93(5)	S7[1]	Na2	S7[6]	89.20(6)
S9	Na1	S6[13]	127.36(7)	S6[6]	Na2	S7[6]	66.66(5)
S1[10]	Na1	S7	101.14(5)	S6[6]	Na2	S7[1]	95.16(7)

[1]x+1/2,-y+3/2,-z+1; [2]x,-y+1/2,z+1/2; [3]-x+1/2,y-1/2,z; [4]-x+1/2,-y+1,z-1/2;

[5]x+1/2,y,-z+1/2; [6]-x+1/2,y+1/2,z;[7]-x+1,-y+1,-z+1; [8]x-1/2,-y+3/2,-z+1;

[9]x,-y+1/2,z-1/2; [10]x-1/2,-y+1/2,-z+1;[11]x+1/2,-y+1/2,-z+1; [12]x,-y+3/2,z-1/2;

[13]-x,-y+1,-z+1; [14]-x+1,y+1/2,-z+3/2;[15] -x+1/2,-y+1,z+1/2; [16] x-1/2,y,-z+1/2;

[17] x,-y+3/2,z+1/2; [18] -x+1,y-1/2,-z+3/2

Table S5. Anisotropic displacement parameters for $Na_4Ga_8S_{14}$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Na1	32(1)	38(1)	22(1)	0(1)	3(1)	-1(1)
Na2	49(1)	54(2)	44(1)	3(1)	8(1)	25(1)
Na3	33(1)	26(1)	49(1)	3(1)	-8(1)	-5(1)
Na4	49(1)	23(1)	34(1)	4(1)	-18(1)	-5(1)
Ga1	12(1)	15(1)	12(1)	0(1)	0(1)	0(1)
Ga2	13(1)	15(1)	12(1)	0(1)	1(1)	-1(1)
Ga3	14(1)	18(1)	15(1)	0(1)	-3(1)	0(1)
Ga4	15(1)	16(1)	12(1)	-1(1)	-2(1)	1(1)
Ga5	12(1)	16(1)	13(1)	0(1)	0(1)	-1(1)
Ga6	15(1)	14(1)	12(1)	-1(1)	1(1)	0(1)
Ga7	14(1)	12(1)	14(1)	0(1)	0(1)	0(1)
Ga8	12(1)	14(1)	14(1)	-1(1)	1(1)	1(1)
S1	14(1)	16(1)	14(1)	-4(1)	0(1)	3(1)
S2	14(1)	21(1)	13(1)	0(1)	1(1)	-4(1)
S3	13(1)	13(1)	13(1)	0(1)	0(1)	0(1)
S4	24(1)	15(1)	13(1)	-2(1)	0(1)	-1(1)
S5	18(1)	15(1)	17(1)	2(1)	-5(1)	-1(1)
S6	20(1)	34(1)	16(1)	-9(1)	-4(1)	12(1)
S7	17(1)	21(1)	16(1)	-4(1)	5(1)	-3(1)
S8	12(1)	14(1)	16(1)	1(1)	2(1)	1(1)
S9	12(1)	13(1)	17(1)	0(1)	-2(1)	0(1)
S10	22(1)	15(1)	12(1)	-1(1)	4(1)	0(1)
S11	15(1)	25(1)	12(1)	-1(1)	0(1)	3(1)
S12	20(1)	15(1)	16(1)	-2(1)	5(1)	-3(1)
S13	14(1)	13(1)	13(1)	0(1)	1(1)	1(1)
S14	17(1)	13(1)	20(1)	0(1)	4(1)	1(1)

Table S6. The quantitative element analyses based on EDS spectrum (Figure S2) in $Na_4Ga_8S_{14}$.

Element	Wt%	Wt% Sigma	Atomic %
Na	8.47	0.23	15.14
S	44.60	0.33	57.19
Ga	46.93	0.35	27.67
Total:	100.00		100.00

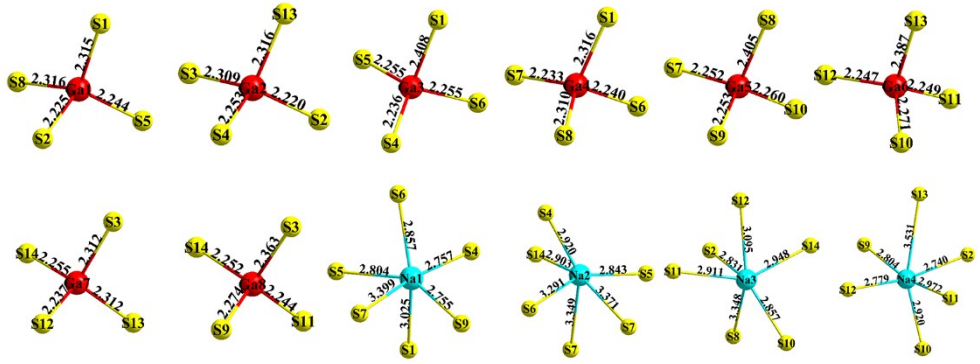

Figure S1. (a) The coordination environments and bond lengths of the $[GaS_4]$ tetrahedral units and $[NaS_6]$ polyhedral groups in $Na_4Ga_8S_{14}$.

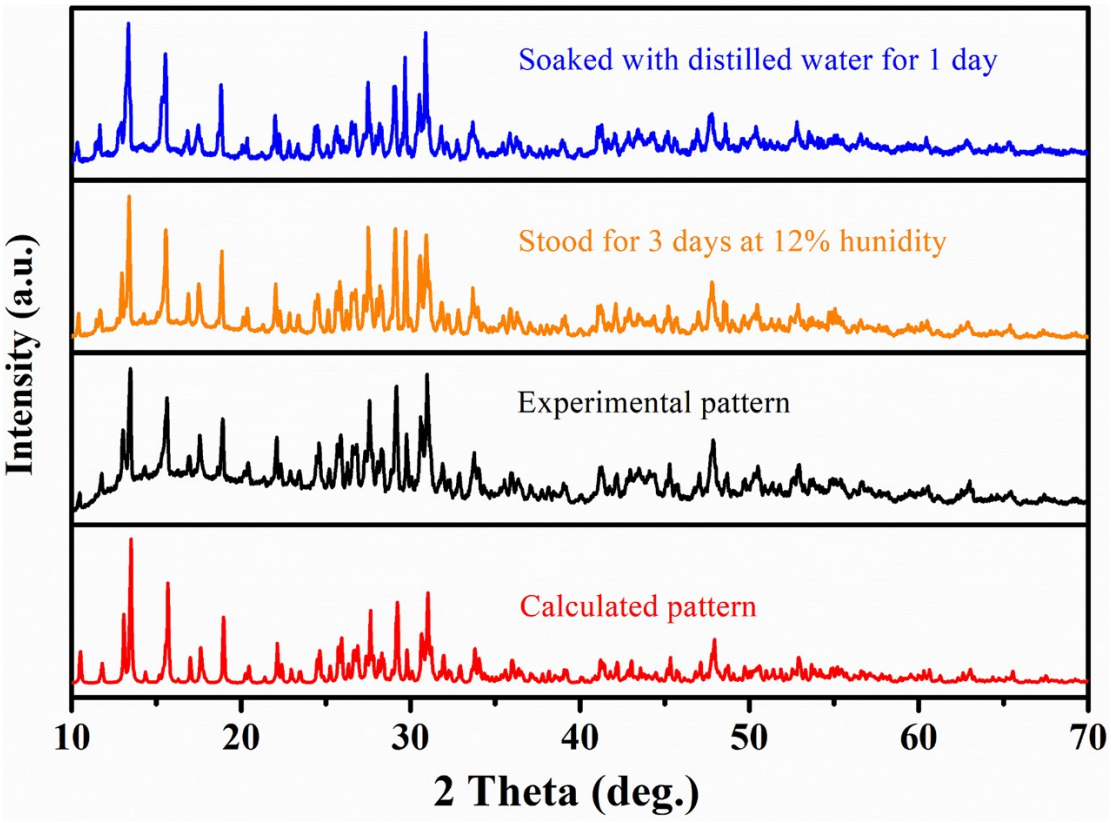

Figure S2. The experimental and theoretical powder X-ray diffraction patterns of $Na_4Ga_8S_{14}$.

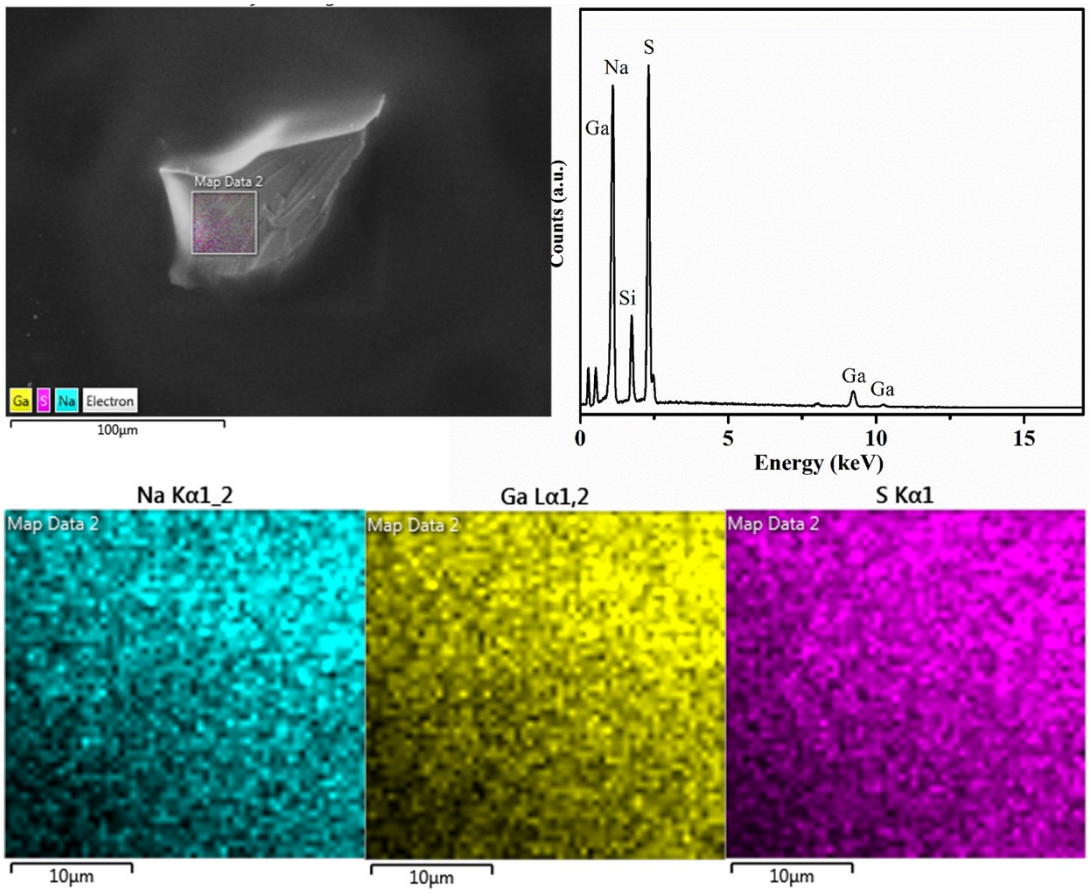

Figure S3. The SEM image, EDS spectrum and mappings of $Na_4Ga_8S_{14}$.