Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

$Na_6Zn_3M^{III}_2Q_9$ (M^{III} = Ga, In; Q = S, Se): four new supertetrahedron-layered chalcogenides with unprecedented vertex-sharing T_3-clusters and desirable photoluminescence performances

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Table S1. Bond lengths (Å) and angles (deg) for $Na_6Zn_3Ga_2S_9$ (M=Zn/Ga).

M(1)-S(5)	2.314(2)	Na(5)-S(6)#7	2.939(4)
M(1)-S(2)	2.327(2)	Na(5)-S(4)#9	3.138(4)
M(1)-S(6)	2.348(2)	Na(5)-S(1)#9	3.139(5)
M(1)-S(8)	2.369(2)	Na(6)-S(5)#12	2.830(6)
M(2)-S(3)	2.338(2)	Na(6)-S(4)#8	2.940(6)
M(2)-S(9)	2.342(2)	Na(6)-S(8)#11	3.368(5)
M(2)-S(7)	2.359(2)	Na(7)-S(2)#10	2.849(7)
M(2)-S(8)	2.390(2)	Na(7)-S(1)#1	3.005(9)
M(3)-S(5)	2.280(2)	S(5)-M(1)-S(2)	109.58(7)
M(3)-S(1)	2.301(2)	S(5)-M(1)-S(6)	106.95(7)
M(3)-S(3)	2.302(2)	S(2)-M(1)-S(6)	106.08(7)
M(3)-S(7)#3	2.3313(19)	S(5)-M(1)-S(8)	113.06(8)
M(4)-S(2)#3	2.272(2)	S(2)-M(1)-S(8)	112.51(7)
M(4)-S(2)	2.272(2)	S(6)-M(1)-S(8)	108.26(7)
M(4)-S(7)	2.3068(19)	S(3)-M(2)-S(9)	107.98(8)
M(4)-S(7)#3	2.3068(19)	S(3)-M(2)-S(7)	110.05(7)
M(5)-S(4)	2.284(2)	S(9)-M(2)-S(7)	106.71(7)
M(5)-S(9)#3	2.285(2)	S(3)-M(2)-S(8)	111.27(7)
M(5)-S(1)	2.298(2)	S(9)-M(2)-S(8)	109.74(7)
M(5)-S(6)#4	2.309(2)	S(7)-M(2)-S(8)	110.94(8)
M(6)-S(4)#3	2.308(2)	S(5)-M(3)-S(1)	106.64(7)
M(6)-S(4)	2.308(2)	S(5)-M(3)-S(3)	108.58(7)
M(6)-S(3)#3	2.3279(19)	S(1)-M(3)-S(3)	109.09(8)
M(6)-S(3)	2.3279(19)	S(5)-M(3)-S(7)#3	108.93(8)
Na(1)-S(7)#13	2.8265(19)	S(1)-M(3)-S(7)#3	109.77(7)
Na(1)-S(1)#12	2.887(2)	S(3)-M(3)-S(7)#3	113.59(7)
Na(1)-S(1)#3	2.887(2)	S(2)#3-M(4)-S(2)	107.74(11)
Na(1)-S(9)#13	2.9039(19)	S(2)#3-M(4)-S(7)	109.82(7)
Na(2)-S(2)#2	2.810(3)	S(2)-M(4)-S(7)	107.84(7)
Na(2)-S(1)#12	2.865(3)	S(2)#3-M(4)-S(7)#3	107.84(7)
Na(2)-S(6)#2	2.898(3)	S(2)-M(4)-S(7)#3	109.82(7)
Na(3)-S(5)#1	2.809(3)	S(7)-M(4)-S(7)#3	113.64(10)
Na(3)-S(4)#14	2.865(3)	S(4)-M(5)-S(9)#3	111.64(7)
Na(3)-S(6)#1	2.907(3)	S(4)-M(5)-S(1)	112.03(8)
Na(4)-S(3)#8	2.8097(19)	S(9)#3-M(5)-S(1)	110.65(8)
Na(4)-S(4)#3	2.8892(19)	S(4)-M(5)-S(6)#4	108.53(8)
Na(4)-S(4)#14	2.8892(19)	S(9)#3-M(5)-S(6)#4	105.83(7)
Na(4)-S(9)#8	2.946(2)	S(1)-M(5)-S(6)#4	107.87(7)
Na(5)-S(9)#6	2.907(4)		

Symmetry transformations used to generate equivalent atoms:

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

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

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

#7 x,-y,z-1/2 #8 -x+1,-y+1,-z+1 #9 -x+1/2,y-1/2,-z+1/2
#10 x,-y,z+1/2 #11 -x+1,y,-z+3/2
#12 x+1/2,-y+1/2,z+1/2 #13 -x+3/2,-y+1/2,-z+1
#14 x,-y+1,z+1/2 #15 -x+1/2,-y+1/2,-z

Table S2. Bond lengths (Å) and angles (deg) for $Na_6Zn_3Ga_2Se_9$ (M=Zn/Ga).

M(1)-Se(5)	2.381(2)	Na(6)-Se(5)#12	2.853(12)
M(1)-Se(2)	2.383(2)	Na(6)-Se(4)#8	3.047(16)
M(1)-Se(6)	2.405(2)	Na(7)-Se(2)#10	2.914(16)
M(1)-Se(8)	2.430(2)	Na(7)-Se(1)#1	3.097(18)
M(2)-Se(3)	2.393(2)	Na(7)-Se(8)#11	3.479(14)
M(2)-Se(9)	2.405(2)	Se(5)-M(1)-Se(2)	109.91(8)
M(2)-Se(7)	2.405(2)	Se(5)-M(1)-Se(6)	106.93(8)
M(2)-Se(8)	2.437(2)	Se(2)-M(1)-Se(6)	105.97(8)
M(3)-Se(5)	2.342(2)	Se(5)-M(1)-Se(8)	112.87(9)
M(3)-Se(3)	2.362(2)	Se(2)-M(1)-Se(8)	112.66(8)
M(3)-Se(1)	2.365(2)	Se(6)-M(1)-Se(8)	108.09(8)
M(3)-Se(7)#3	2.377(2)	Se(3)-M(2)-Se(9)	107.95(9)
M(4)-Se(2)	2.339(2)	Se(3)-M(2)-Se(7)	111.79(8)
M(4)-Se(2)#3	2.339(2)	Se(9)-M(2)-Se(7)	106.95(7)
M(4)-Se(7)	2.3646(19)	Se(3)-M(2)-Se(8)	110.60(8)
M(4)-Se(7)#3	2.3646(19)	Se(9)-M(2)-Se(8)	109.08(8)
M(5)-Se(9)#3	2.349(2)	Se(7)-M(2)-Se(8)	110.34(9)
M(5)-Se(4)	2.357(2)	Se(5)-M(3)-Se(3)	109.28(8)
M(5)-Se(1)	2.363(2)	Se(5)-M(3)-Se(1)	105.35(7)
M(5)-Se(6)#4	2.379(2)	Se(3)-M(3)-Se(1)	108.58(9)
M(6)-Se(4)#3	2.373(2)	Se(5)-M(3)-Se(7)#3	108.34(9)
M(6)-Se(4)	2.373(2)	Se(3)-M(3)-Se(7)#3	114.15(8)
M(6)-Se(3)	2.3736(19)	Se(1)-M(3)-Se(7)#3	110.75(8)
M(6)-Se(3)#3	2.3736(19)	Se(2)-M(4)-Se(2)#3	106.42(12)
Na(1)-Se(7)#13	2.8685(14)	Se(2)-M(4)-Se(7)	108.75(5)
Na(1)-Se(1)#3	2.9540(16)	Se(2)#3-M(4)-Se(7)	109.13(5)
Na(1)-Se(1)#12	2.9540(16)	Se(2)-M(4)-Se(7)#3	109.13(5)
Na(1)-Se(9)#13	2.9888(15)	Se(2)#3-M(4)-Se(7)#3	108.75(5)
Na(2)-Se(2)#2	2.865(6)	Se(7)-M(4)-Se(7)#3	114.36(12)
Na(2)-Se(1)#12	2.927(6)	Se(9)#3-M(5)-Se(4)	111.52(8)
Na(2)-Se(6)#2	2.977(6)	Se(9)#3-M(5)-Se(1)	111.16(9)
Na(3)-Se(5)#1	2.860(5)	Se(4)-M(5)-Se(1)	112.54(8)
Na(3)-Se(4)#14	2.910(6)	Se(9)#3-M(5)-Se(6)#4	105.46(8)
Na(3)-Se(6)#1	2.973(6)	Se(4)-M(5)-Se(6)#4	108.24(9)
Na(4)-Se(3)#8	2.8537(15)	Se(1)-M(5)-Se(6)#4	107.54(8)
Na(4)-Se(4)#14	2.9481(14)	Se(4)#3-M(6)-Se(4)	105.00(12)
Na(4)-Se(4)#3	2.9481(14)	Se(4)#3-M(6)-Se(3)	110.87(5)

Na(4)-Se(9)#8	3.0122(15)	Se(4)-M(6)-Se(3)	107.88(5)
Na(5)-Se(9)#6	2.974(7)	Se(4)#3-M(6)-Se(3)#3	107.88(5)
Na(5)-Se(6)#7	2.976(7)	Se(4)-M(6)-Se(3)#3	110.87(5)
Na(5)-Se(1)#9	3.166(9)	Se(3)-M(6)-Se(3)#3	113.98(12)
Na(5)-Se(4)#9	3.186(7)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,-y+1/2,-z+1 #2 -x+1,-y,-z+1
#3 -x+1,y,-z+1/2 #4 -x+1/2,y+1/2,-z+1/2
#5 x,-y+1,z-1/2 #6 x-1/2,-y+1/2,z-1/2
#7 x,-y,z-1/2 #8 -x+1,-y+1,-z+1 #9 -x+1/2,y-1/2,-z+1/2
#10 x,-y,z+1/2 #11 -x+1,y,-z+3/2
#12 x+1/2,-y+1/2,z+1/2 #13 -x+3/2,-y+1/2,-z+1

Table S3. Bond lengths (Å) and angles (deg) for $Na_6Zn_3In_2S_9$ (H=Zn/In).

H(1)-S(5)	2.4236(19)	Na(6)-S(5)#13	2.809(6)
H(1)-S(2)	2.4303(19)	Na(6)-S(4)#9	3.071(8)
H(1)-S(6)	2.4505(18)	Na(6)-S(8)#12	3.271(5)
H(1)-S(8)	2.4561(19)	Na(7)-S(2)#11	2.745(10)
H(2)-S(9)	2.369(2)	Na(7)-S(1)#1	3.226(16)
H(2)-S(3)	2.3764(19)	Na(7)-S(8)#12	3.331(10)
H(2)-S(7)	2.383(2)	S(5)-H(1)-S(2)	109.95(7)
H(2)-S(8)	2.439(2)	S(5)-H(1)-S(6)	107.00(7)
H(3)-S(1)	2.3622(19)	S(2)-H(1)-S(6)	106.79(7)
H(3)-S(5)	2.3657(19)	S(5)-H(1)-S(8)	111.81(7)
H(3)-S(3)	2.3756(19)	S(2)-H(1)-S(8)	112.77(7)
H(3)-S(7)#3	2.3829(19)	S(6)-H(1)-S(8)	108.22(7)
H(4)-S(2)	2.3619(19)	S(9)-H(2)-S(3)	109.51(7)
H(4)-S(2)#3	2.3619(19)	S(9)-H(2)-S(7)	108.73(7)
H(4)-S(7)	2.3721(18)	S(3)-H(2)-S(7)	112.10(7)
H(4)-S(7)#3	2.3721(18)	S(9)-H(2)-S(8)	104.10(7)
H(5)-S(4)	2.4258(19)	S(3)-H(2)-S(8)	110.59(7)
H(5)-S(9)#3	2.4304(19)	S(7)-H(2)-S(8)	111.47(7)
H(5)-S(1)	2.4312(19)	S(1)-H(3)-S(5)	103.99(7)
H(5)-S(6)#4	2.4682(18)	S(1)-H(3)-S(3)	110.89(7)
H(6)-S(4)#3	2.3671(19)	S(5)-H(3)-S(3)	107.51(7)
H(6)-S(4)	2.3671(19)	S(1)-H(3)-S(7)#3	110.27(7)
H(6)-S(3)	2.3922(18)	S(5)-H(3)-S(7)#3	109.77(7)
H(6)-S(3)#3	2.3922(18)	S(3)-H(3)-S(7)#3	113.90(7)
Na(1)-S(7)#14	2.8511(17)	S(2)-H(4)-S(2)#3	105.04(10)
Na(1)-S(1)#3	2.935(2)	S(2)-H(4)-S(7)	106.79(6)
Na(1)-S(1)#13	2.935(2)	S(2)#3-H(4)-S(7)	111.31(6)
Na(1)-S(9)#14	3.006(2)	S(2)-H(4)-S(7)#3	111.31(6)
Na(2)-S(2)#2	2.848(3)	S(2)#3-H(4)-S(7)#3	106.79(6)

Na(2)-S(1)#13	2.853(3)	S(7)-H(4)-S(7)#3	115.18(10)
Na(2)-S(6)#2	2.997(4)	S(4)-H(5)-S(9)#3	110.97(7)
Na(3)-S(5)#1	2.853(3)	S(4)-H(5)-S(1)	113.12(7)
Na(3)-S(4)#15	2.864(4)	S(9)#3-H(5)-S(1)	111.79(7)
Na(3)-S(6)#1	2.996(4)	S(4)-H(5)-S(6)#4	108.20(7)
Na(4)-S(3)#9	2.8428(18)	S(9)#3-H(5)-S(6)#4	103.50(6)
Na(4)-S(4)#3	2.9289(19)	S(1)-H(5)-S(6)#4	108.73(6)
Na(4)-S(4)#15	2.9289(19)	S(4)#3-H(6)-S(4)	104.47(10)
Na(4)-S(9)#9	3.037(2)	S(4)#3-H(6)-S(3)	110.26(6)
Na(5)-S(6)#8	2.852(5)	S(4)-H(6)-S(3)	109.59(6)
Na(5)-S(9)#5	2.974(5)	S(4)#3-H(6)-S(3)#3	109.59(6)
Na(5)-S(1)#10	3.231(6)	S(4)-H(6)-S(3)#3	110.26(6)
Na(5)-S(4)#10	3.264(6)	S(3)-H(6)-S(3)#3	112.38(10)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,-y+1/2,-z+1 #2 -x+1,-y,-z+1
#3 -x+1,y,-z+1/2 #4 -x+1/2,y+1/2,-z+1/2
#5 x-1/2,-y+1/2,z-1/2 #6 x,-y+1,z-1/2
#7 -x+1/2,-y+1/2,-z #8 x,-y,z-1/2
#9 -x+1,-y+1,-z+1 #10 -x+1/2,y-1/2,-z+1/2
#11 x,-y,z+1/2 #12 -x+1,y,-z+3/2
#13 x+1/2,-y+1/2,z+1/2 #14 -x+3/2,-y+1/2,-z+1
#15 x,-y+1,z+1/2

Table S4. Bond lengths (Å) and angles (deg) for $Na_6Zn_3In_2Se_9$ (H=Zn/In)

H(1)-Se(5)	2.5469(14)	Na(6)-Se(5)#12	2.982(15)
H(1)-Se(2)	2.5483(13)	Na(6)-Se(4)#8	3.167(16)
H(1)-Se(8)	2.5806(13)	Na(6)-Se(8)#11	3.332(11)
H(1)-Se(6)	2.5817(13)	Na(7)-Se(2)#10	2.975(18)
H(2)-Se(9)	2.5057(15)	Na(7)-Se(1)#1	3.22(3)
H(2)-Se(3)	2.5064(15)	Na(7)-Se(8)#11	3.358(15)
H(2)-Se(7)	2.5085(14)	Se(5)-H(1)-Se(2)	110.65(4)
H(2)-Se(8)	2.5619(14)	Se(5)-H(1)-Se(8)	112.47(5)
H(3)-Se(1)	2.4670(15)	Se(2)-H(1)-Se(8)	113.14(5)
H(3)-Se(5)	2.4686(15)	Se(5)-H(1)-Se(6)	107.24(5)
H(3)-Se(3)	2.4857(15)	Se(2)-H(1)-Se(6)	107.36(4)
H(3)-Se(7)#3	2.4908(14)	Se(8)-H(1)-Se(6)	105.56(4)
H(4)-Se(2)#3	2.4660(14)	Se(9)-H(2)-Se(3)	109.65(5)
H(4)-Se(2)	2.4660(14)	Se(9)-H(2)-Se(7)	109.41(5)
H(4)-Se(7)	2.4821(13)	Se(3)-H(2)-Se(7)	113.61(5)
H(4)-Se(7)#3	2.4821(13)	Se(9)-H(2)-Se(8)	102.64(5)
H(5)-Se(1)	2.5489(13)	Se(3)-H(2)-Se(8)	110.29(5)
H(5)-Se(4)	2.5512(14)	Se(7)-H(2)-Se(8)	110.69(5)
H(5)-Se(9)#3	2.5609(13)	Se(1)-H(3)-Se(5)	103.61(5)

H(5)-Se(6)#4	2.5991(13)	Se(1)-H(3)-Se(3)	109.84(6)
H(6)-Se(4)#3	2.4719(14)	Se(5)-H(3)-Se(3)	108.48(5)
H(6)-Se(4)	2.4719(14)	Se(1)-H(3)-Se(7)#3	111.02(5)
H(6)-Se(3)#3	2.4982(13)	Se(5)-H(3)-Se(7)#3	108.99(6)
H(6)-Se(3)	2.4982(13)	Se(3)-H(3)-Se(7)#3	114.32(5)
Na(1)-Se(7)#13	2.9695(11)	Se(2)#3-H(4)-Se(2)	104.23(8)
Na(1)-Se(1)#12	3.0755(12)	Se(2)#3-H(4)-Se(7)	109.92(4)
Na(1)-Se(1)#3	3.0755(12)	Se(2)-H(4)-Se(7)	108.40(4)
Na(1)-Se(9)#13	3.1519(12)	Se(2)#3-H(4)-Se(7)#3	108.40(4)
Na(2)-Se(2)#2	2.953(4)	Se(2)-H(4)-Se(7)#3	109.92(4)
Na(2)-Se(1)#12	2.999(5)	Se(7)-H(4)-Se(7)#3	115.39(8)
Na(2)-Se(6)#2	3.136(5)	Se(1)-H(5)-Se(4)	113.07(5)
Na(3)-Se(5)#1	2.949(4)	Se(1)-H(5)-Se(9)#3	112.46(5)
Na(3)-Se(4)#14	2.997(5)	Se(4)-H(5)-Se(9)#3	111.76(5)
Na(3)-Se(6)#1	3.134(5)	Se(1)-H(5)-Se(6)#4	108.52(5)
Na(4)-Se(3)#8	2.9668(11)	Se(4)-H(5)-Se(6)#4	108.07(5)
Na(4)-Se(4)#14	3.0692(12)	Se(9)#3-H(5)-Se(6)#4	102.26(4)
Na(4)-Se(4)#3	3.0692(12)	Se(4)#3-H(6)-Se(4)	103.43(7)
Na(4)-Se(9)#8	3.1638(12)	Se(4)#3-H(6)-Se(3)#3	109.02(4)
Na(5)-Se(6)#7	3.018(6)	Se(4)-H(6)-Se(3)#3	110.88(4)
Na(5)-Se(9)#5	3.073(6)	Se(4)#3-H(6)-Se(3)	110.88(4)
Na(5)-Se(4)#9	3.340(7)	Se(4)-H(6)-Se(3)	109.02(4)
Na(5)-Se(1)#9	3.355(7)	Se(3)#3-H(6)-Se(3)	113.18(7)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,-y+1/2,-z+1 #2 -x+1,-y,-z+1
#3 -x+1,y,-z+1/2 #4 -x+1/2,y+1/2,-z+1/2
#5 x-1/2,-y+1/2,z-1/2 #6 x,-y+1,z-1/2
#7 x,-y,z-1/2 #8 -x+1,-y+1,-z+1 #9 -x+1/2,y-1/2,-z+1/2
#10 x,-y,z+1/2 #11 -x+1,y,-z+3/2
#12 x+1/2,-y+1/2,z+1/2 #13 -x+3/2,-y+1/2,-z+1
#14 x,-y+1,z+1/2

Table S5. Average EDS data of $Na_6Zn_3Ga_2S_9$.

Element	Weight %	Atomic %	Formula
S	36.69	43.42	8.71
Zn	27.51	15.93	3.2
Ga	16.67	9.1	1.82
Na	19.13	31.55	6.33

Formula : $Na_{6.33}Zn_{3.2}Ga_{1.82}S_{8.71}$

Table S6. Average EDS data of $Na_6Zn_3Ga_2Se_9$.

Element	Weight %	Atomic %	Formula
Se	61.3	45.58	9.13
Zn	15.96	14.32	2.87
Ga	10.49	8.84	1.77
Na	12.25	31.26	6.26

Formula : $Na_{6.26}Zn_{2.87}Ga_{1.77}S_{9.13}$

Table S7. Average EDS data of $Na_6Zn_3In_2S_9$.

Element	Weight %	Atomic %	Formula
S	34.94	45.58	9.22
Zn	22.73	14.53	2.94
In	25.51	9.29	1.88
Na	16.82	30.6	6.19

Formula : $Na_{6.19}Zn_{2.94}Ga_{1.88}S_{9.22}$

Table S8. Average EDS data of $Na_6Zn_3In_2Se_9$.

Element	Weight %	Atomic %	Formula
Se	54.8	44.09	8.84
Zn	17.05	16.56	3.32
In	17.39	9.62	1.93
Na	10.76	29.73	5.96

Formula : $Na_{5.96}Zn_{3.32}In_{1.93}Se_{8.84}$

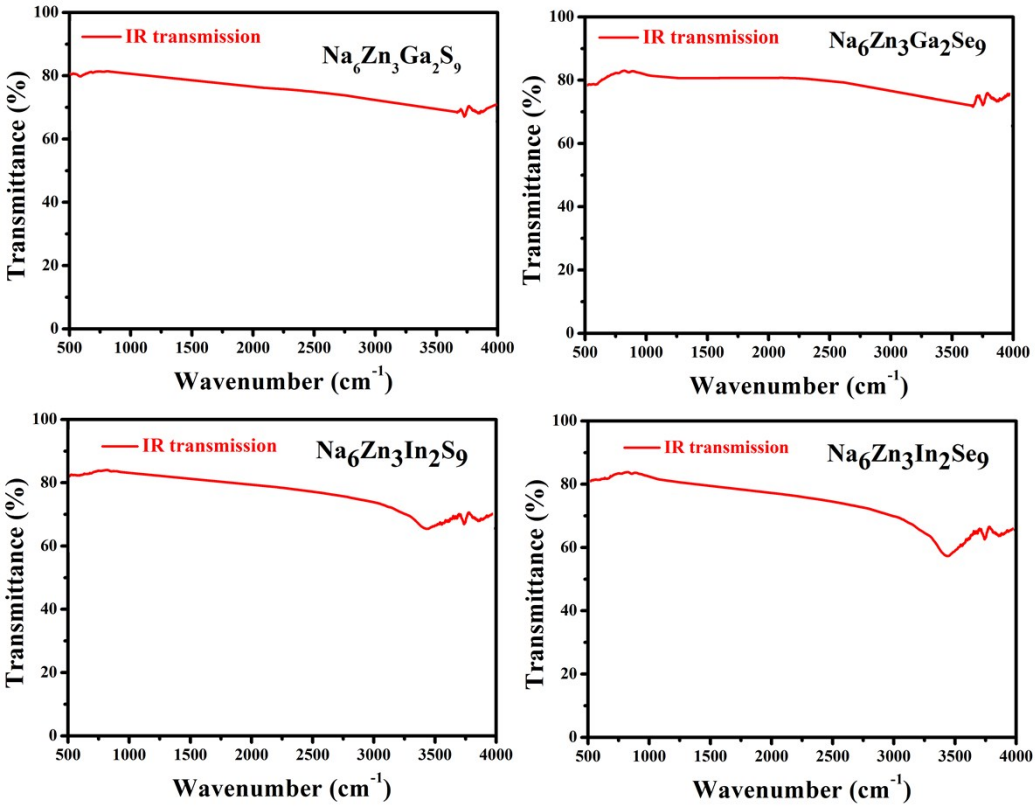

Figure S1. IR spectra of title compounds.

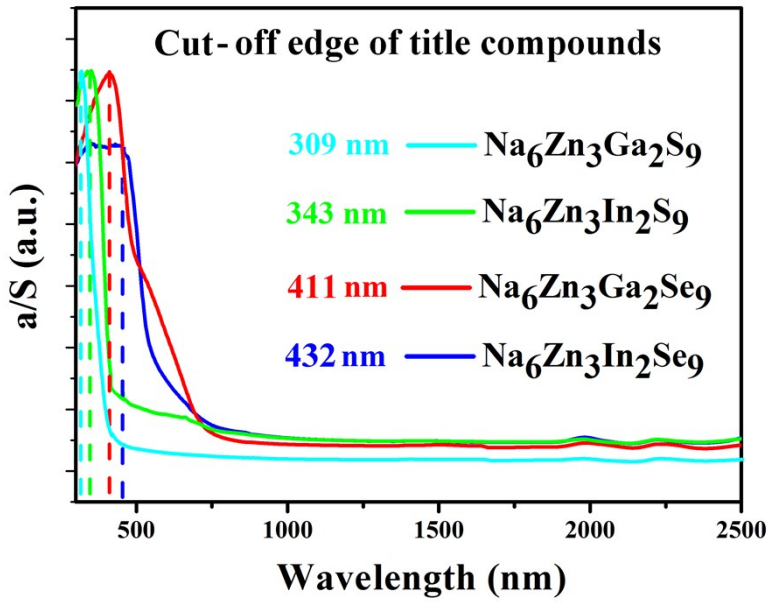

Figure S2. Cut-off edges of title compounds

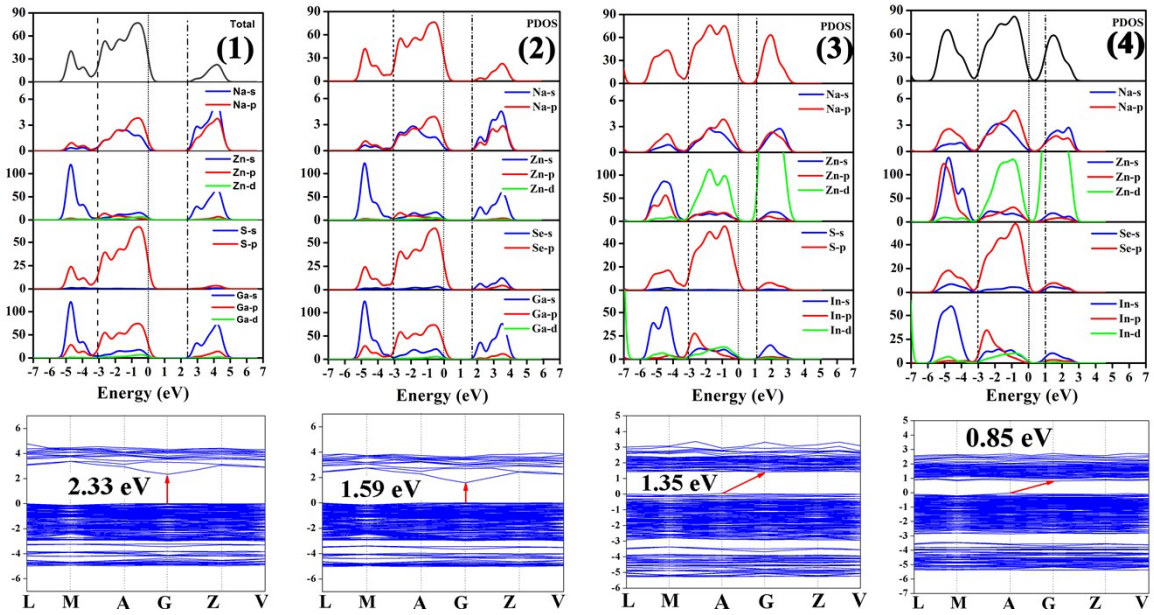

Figure S3. Calculated band structures and PDOS for title compounds; (1) $Na_6Zn_3Ga_2S_9$, (2) $Na_6Zn_3Ga_2Se_9$, (3) $Na_6Zn_3In_2S_9$; (4) $Na_6Zn_3In_2Se_9$.