Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Structural Insights into T2-cluster-containing Chalcogenides with vertex-, edge- and face-sharing connection modes of NaQ_6 ligands: $Na_3ZnM^{III}Q_4$ (M^{III} = In, Ga; Q =S, Se)

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Supporting information

1. Tables and Figures

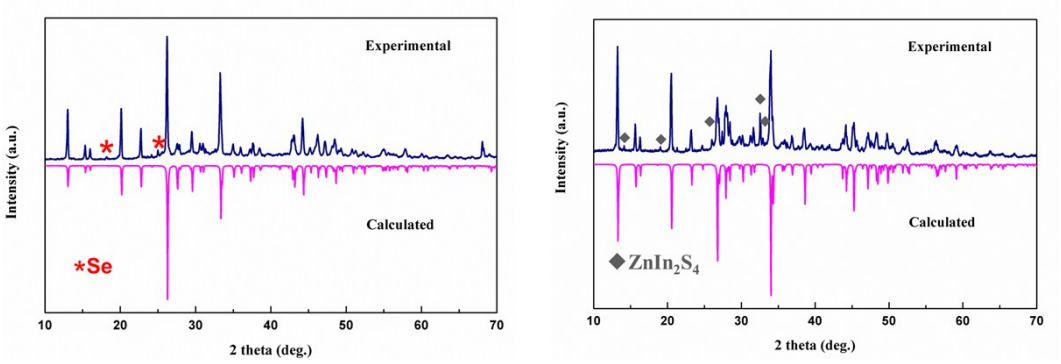
Table S1. A series of NaS_n connection mode in Na-based quaternary sulfides

No.	Compounds	Space group	NaS_n Connection mode
1	$(Cu_{0.644}Na_{0.356})(In_5S_8)$	$F\bar{4}3m$	isolate
2	$(Na_{0.5}Cu_{0.5}In)In_4S_8$	$F\bar{4}3m$	isolate
3	$NaAl(P_2S_6)$	*Fdd2*	isolate
4	$NaScP_2S_6$	*Fdd2*	isolate
5	$NaNdGa_4S_8$	*Fddd*	isolate
6	$Na_{0.5}Nd_{0.5}Ga_2S_4$	*Fddd*	isolate
7	$CeGa_4NaS_8$	*Fddd*	isolate
8	$Na_{0.5}La_{0.5}Ga_2S_4$	*Fddd*	isolate
9	$Na_{0.66}Eu_{2.86}As_{4.54}S_{10}$	$P2_1/c$	isolate
10	$Na_{2.9}KMo_{12}S_{14}$	$P\bar{3}1c$	isolate
11	$NaAsEuS_4$	*Ama2*	sharing corners
12	$Na_2(CdSnS_4)$	*C2*	sharing corners
13	$NaBa_2Cu_3S_5$	*C2/m*	sharing corners
14	$Ga_2Na_2SnS_6$	*Cc*	sharing corners
15	$Na_2Ge_2CdS_6$	*Cc*	sharing corners
16	$In_2Na_2SiS_6$	*Cc*	sharing corners
17	$GeIn_2Na_2S_6$	*Cc*	sharing corners
18	$Na_2In_2SiS_6$	*Cc*	sharing corners
19	$Na_2In_2GeS_6$	*Cc*	sharing corners
20	$Na_2ZnGe_2S_6$	*Cc*	sharing corners
21	$Na_2CdGe_2S_6$	*Cc*	sharing corners
22	$Na_{1.26}Ga_{1.26}Sn_{0.74}S_4$	*Fdd2*	sharing corners
23	$Na_2Sn_2ZnS_6$	*Fdd2*	sharing corners
24	$Na_6Pb_3(PS_4)_4$	*R3mH*	sharing corners

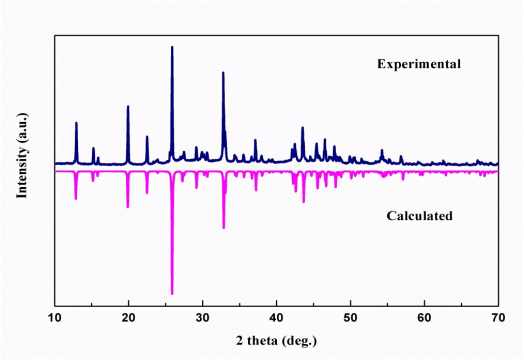
25	$Na(Nb_2PS_{10})$	*C2/c*	sharing edges
26	$Na_8Pb_2(Ge_2S_6)_2$	*C2/m*	sharing edges
27	$Na_8Sn_2(Ge_2S_6)_2$	*C2/m*	sharing edges
28	$Na_6(CdSn_4S_{12})$	*C2/m*	sharing edges
29	$Ge_2Na_2ZnS_6$	*Cc*	sharing edges
30	$Ga_2GeNa_2S_6$	*Fdd2*	sharing edges
31	$Ga_2Na_2SnS_6$	*Fdd2*	sharing edges
32	$NaPd(PS_4)$	*I4/mc*	sharing edges
33	$NaYb(P_2S_6)$	$P\bar{1}$	sharing edges
34	$NaErP_2S_6$	$P\bar{1}$	sharing edges
35	$NaLuP_2S_6$	$P\bar{1}$	sharing edges
36	$NaTbP_2S_6$	$P\bar{1}$	sharing edges
37	$NaYP_2S_6$	$P\bar{1}$	sharing edges
38	$NaSb(P_2S_6)$	$P2_1$	sharing edges
39	$Na(Na_{0.5}Ag_{0.5})TeS_3$	$P2_1/c$	sharing edges
40	$NaSb(P_2S_6)$	$P2_1/c$	sharing edges
41	$Na_4As_4Eu_2S_{10}$	$P2_1/c$	sharing edges
42	$Na(CuFe)_{1.053}S_2$	$P\bar{3}m1$	sharing edges
43	$LiNaZnS_2$	$P\bar{3}m1$	sharing edges
44	$LiNaCdS_2$	$P\bar{3}m1$	sharing edges
45	$Na(LiMn)S_2$	$P\bar{3}m1$	sharing edges
46	$NaTi_2(PS_4)_3$	*P6cc*	sharing edges
47	$NaGaSnS_4$	*Pa-3*	sharing edges
48	$Na_{0.6}(Ti_{0.4}V_{0.6})S_2$	*R3mH*	sharing edges
49	$Na_{0.7}Cr_{0.}7Ti_{0.}3S_2$	*R3mH*	sharing edges
50	$Na_{0.95}Zr_2N_2S_{1.836}$	$R\bar{3}mH$	sharing edges
51	$Na_{0.9}Cr_{0.9}Ti_{0.1}S_2$	$R\bar{3}mH$	sharing edges

52	$Na_{0.5}(Y_{0.5}Zr_{0.5})S_2$	$R\bar{3}_mH$	sharing edges
53	Na2Cu(SbS3)	*P21/n*	sharing edges
54	$Na_8Eu_2(Si_2S_6)_2$	*C2/m*	sharing faces
55	$Na_8Eu_2(Ge_2S_6)_2$	*C2/m*	sharing faces
56	$Na_5(CoS_{2)2}Br$	*I4mm*	sharing faces
57	$(NaInSnS_4)_{0.5}$	*P6/m*	sharing faces
58	$La_6(GaNa)Ga_2S_{14}$	$P6_3$	sharing faces
59	$NaY_3S_3(SiS_4)$	$P6_3$	sharing faces
60	$NaSm_3S_3(SiS_4)$	$P6_3$	sharing faces
61	$NaYb_3GeS_7$	$P6_3$	sharing faces
62	$NaSm_3GeS_7$	$P6_3$	sharing faces
63	$NaNd_3GeS_7$	$P6_3$	sharing faces
64	$NaGd_3GeS_7$	$P6_3$	sharing faces
65	$NaCe_3GeS_7$	$P6_3$	sharing faces
66	$Na_{2.54}Cs_{1.14}Mo_9S_{11}$	$P6_3/m$	sharing faces
67	$Na(Cu_2NbS_4)$	*Ama2*	sharing corners and edges
68	$NaCdSbS_3$	*C2/c*	sharing corners and edges
69	$(Li_{0.60}Na_{0.40})AsS_2$	*Cc*	sharing corners and edges
70	$NaSm(P_2S_6)$	$P2_1/a$	sharing corners and edges
71	$Na_3(Cr_2P_3S_{12})$	$P2_1/c$	sharing corners and edges
72	$NaPrP_2S_6$	$P2_1/c$	sharing corners and edges
73	$Na_{0.16}Bi_{1.28}(P_2S_6)$	$P2_1/n$	sharing corners and edges
74	NaBaVS4	$P2_1/n$	sharing corners and edges
75	$NaCdAsS_3$	$P2_1/n$	sharing corners and edges
76	$Na_8Cu_4Nb_2S_{21}$	$P2_12_12$	sharing corners and edges
77	$(NaLi)As_2S_4$	*Pbca*	sharing corners and edges
78	$Na_4In_8S_2Se_{12}$	$Pca2_1$	sharing corners and edges

79	$Na_9Gd_5Sb_8(S_2)_2S_{22}$	*Pnma*	sharing corners and edges
80	Na3PS3Se	*P421c*	sharing corners and faces
81	$NaCuZrS_3$	*Cmcm*	sharing corners and faces
82	$Na_{0.5}Pb_{1.75}(GeS_4)$	$I\bar{4}3d$	sharing corners and faces
83	$Na_6Pb_3(PS_4)_4$	$I\bar{4}3d$	sharing corners and faces
84	$Na((Cu_{1.54}V_{0.46})S_2)$	$P\bar{3}$	sharing corners and faces
85	$NaCuTiS_3$	*Pnma*	sharing corners and faces
86	$Na_2(Cu_2ZrS_4)$	*C2/m*	sharing edges and faces
87	$Na_5AgGe_2S_7$	*C2/c*	sharing corners ,edges
88	$Na_5Li_3Ti_2S_8$	*C2/c*	sharing corners ,edges
89	$Na_{1.515}EuGeS_4$	*R3cH*	sharing corners ,edges



(a) (b)



(c)

Figure S1. Powder X-ray diffraction patterns of (a) $Na_3ZnGaSe_4$, (b) Na_3ZnInS_4, (c) $Na_3ZnInSe_4$.

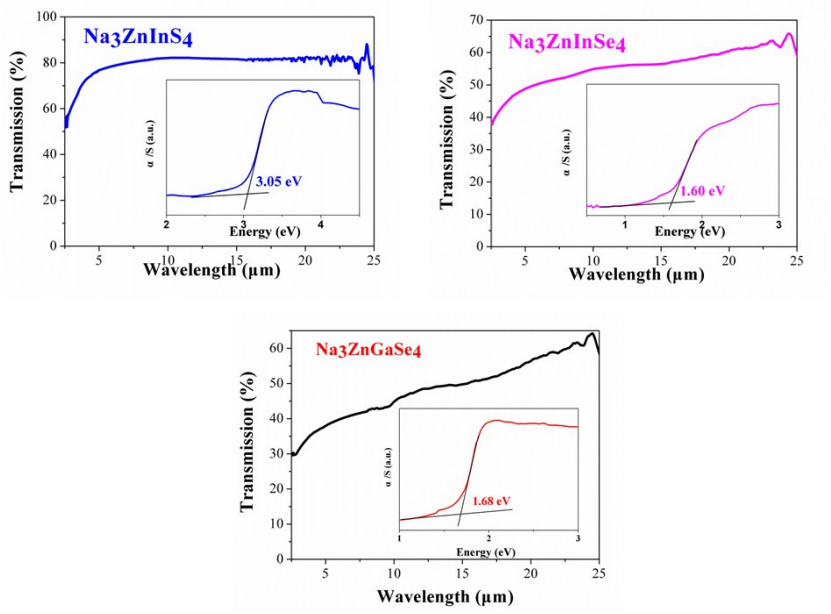


Figure S2. IR and diffuse-reflectance spectra of $Na_3ZnGaSe_4$, Na_3ZnInS_4, $Na_3ZnInSe_4$.

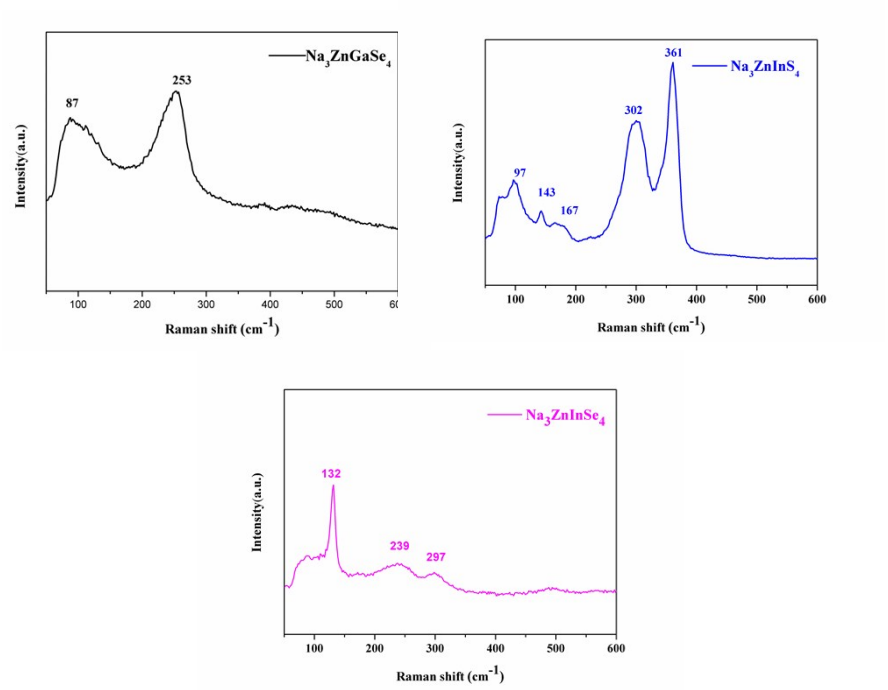
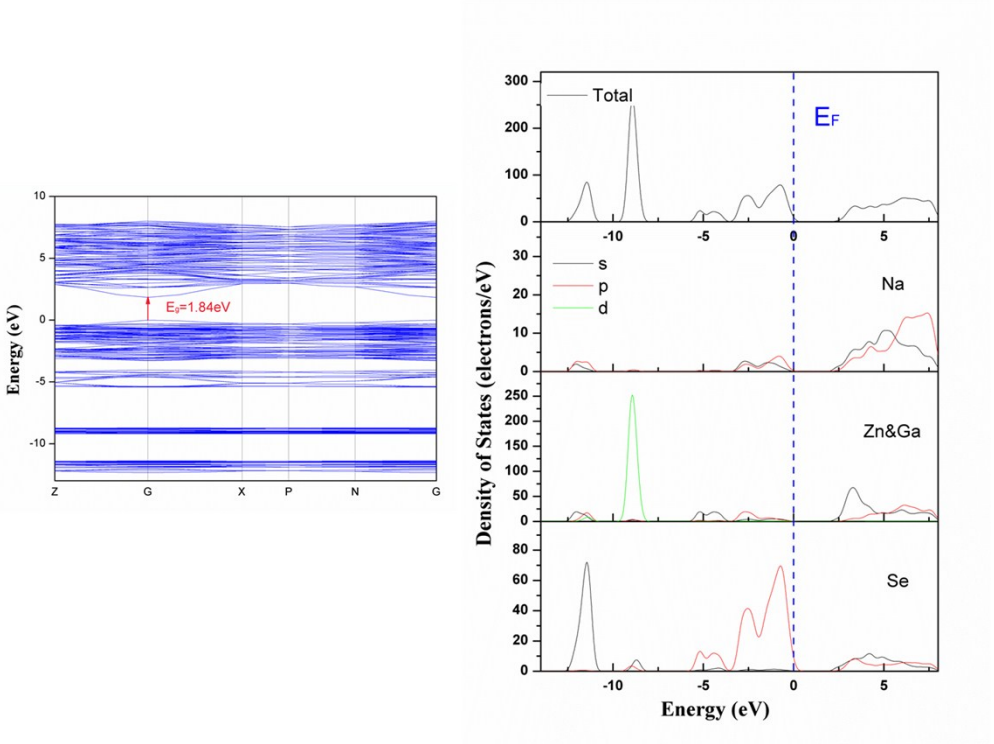
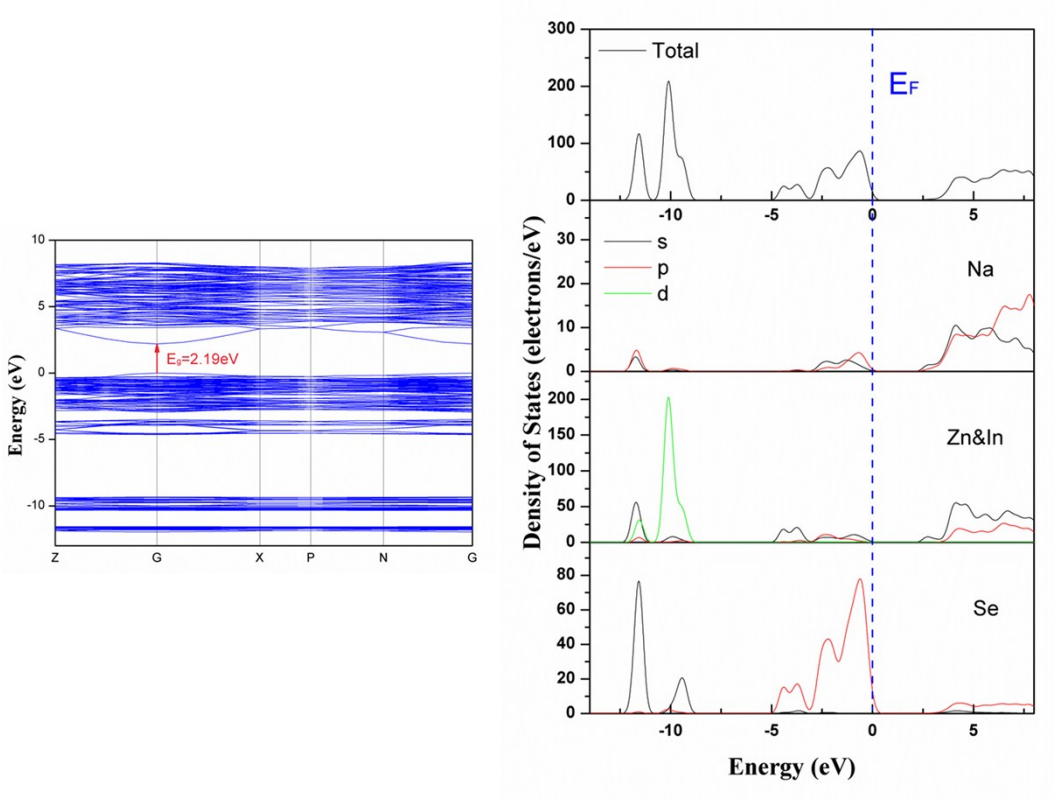


Figure S3. Raman spectra of $Na_3ZnGaSe_4$, Na_3ZnInS_4, $Na_3ZnInSe_4$



（a）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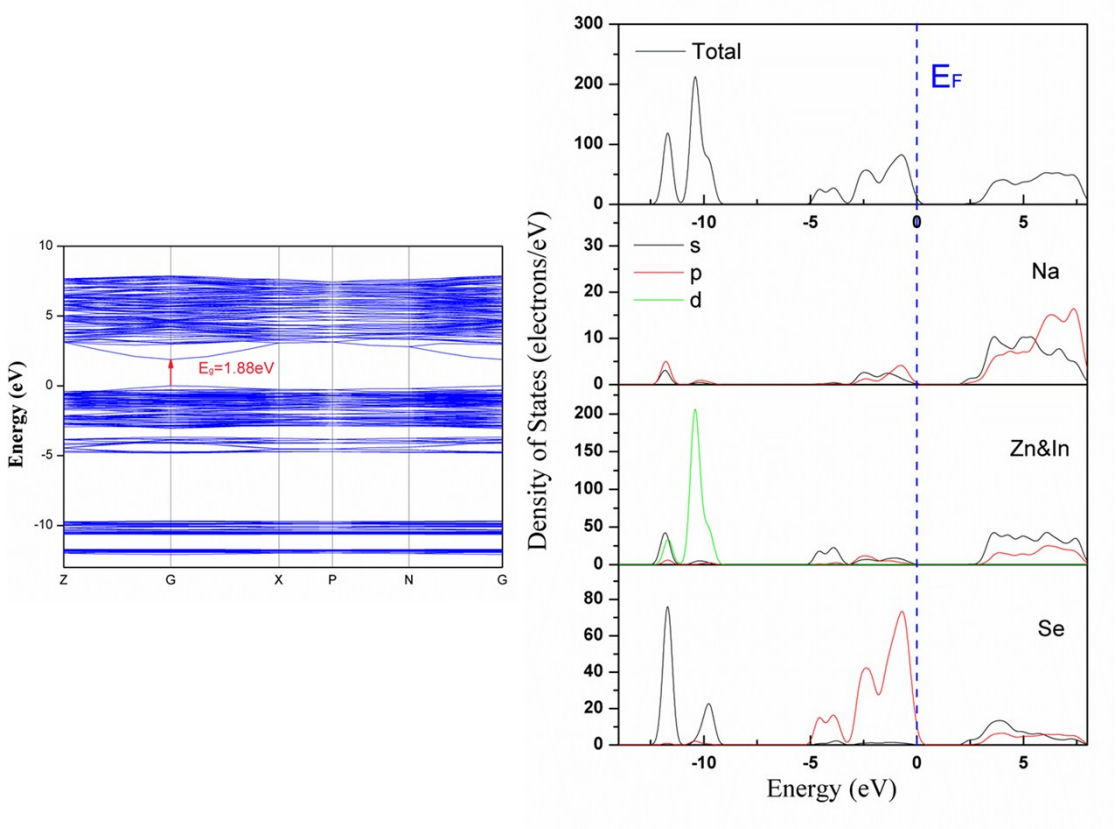
G
X
P
N
G
Total
E_F
s
p
d
Na
Zn&In
Se
Density of States (electrons/eV)
Energy (eV)

(b)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G
X
P
N
G
Total
E_F
s
p
d
Na
Zn&In
Se
Density of States (electrons/eV)
Energy (eV)

（c）

Figure S4. Band structures, PDOS and TDOS plots of (a) $Na_3ZnGaSe_4$, (b) Na_3ZnInS_4, (c) $Na_3ZnInSe_4$.

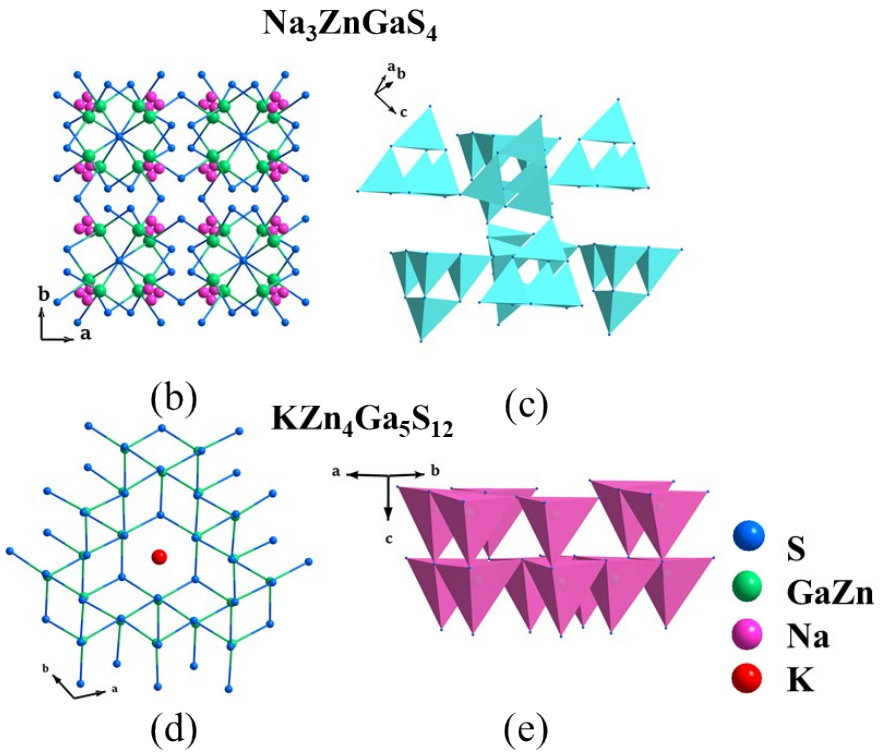

Figure S5. Overall structure of Na_3ZnGaS_4 and $KZn_4Ga_5S_{12}$.

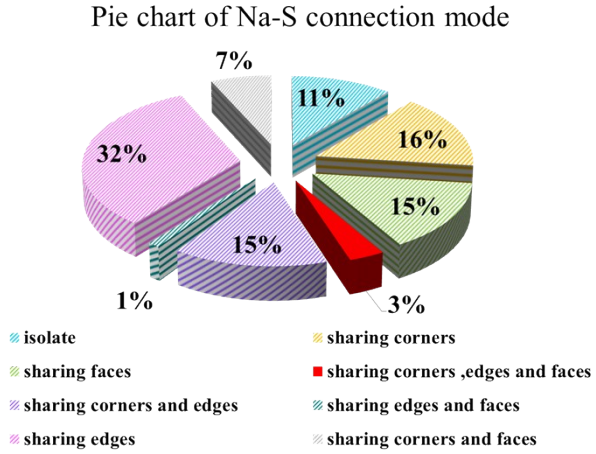

Figure S6. Pie chart of NaSn connection mode..

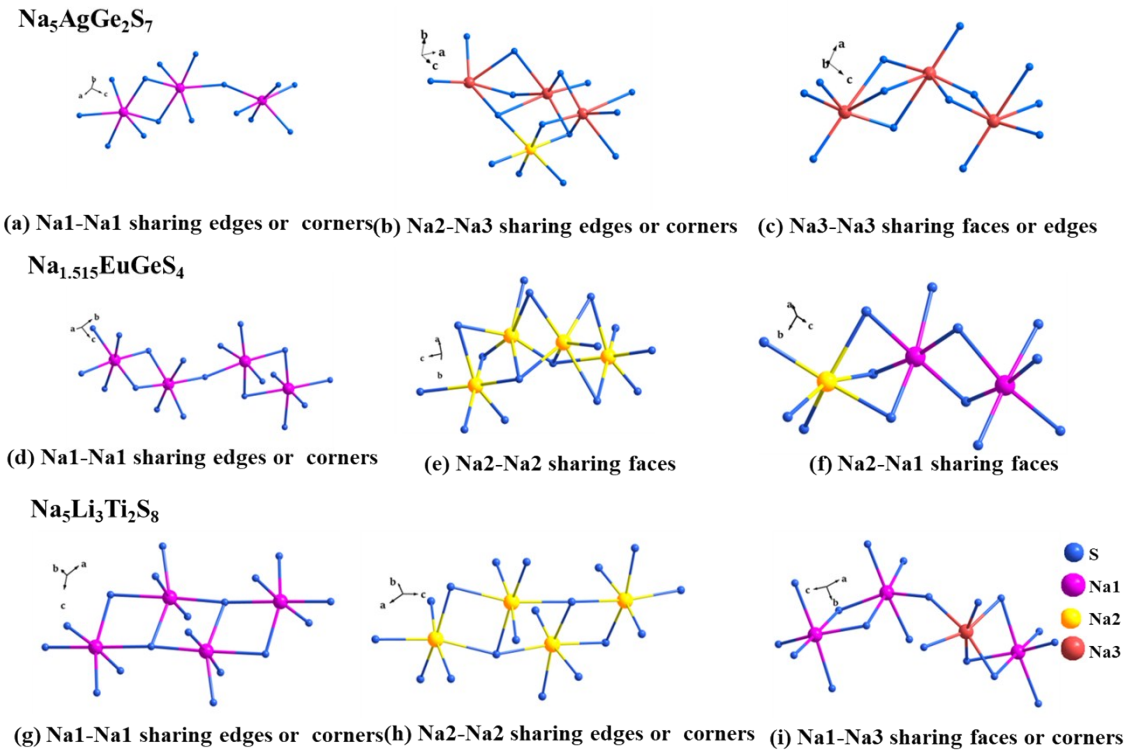

Figure S7. Connection modes of NaS_n ligands in the $Na_5AgGe_2S_7$, $Na_{1.515}EuGeS_4$ and $Na_5Li_3Ti_2S_8$;