Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Synthesis, Structural Evolution and Optical Properties of a New Family of Oxychalcogenides $[Sr_3VO_4][MQ_3]$ (M = Ga, In, Q = S, Se)

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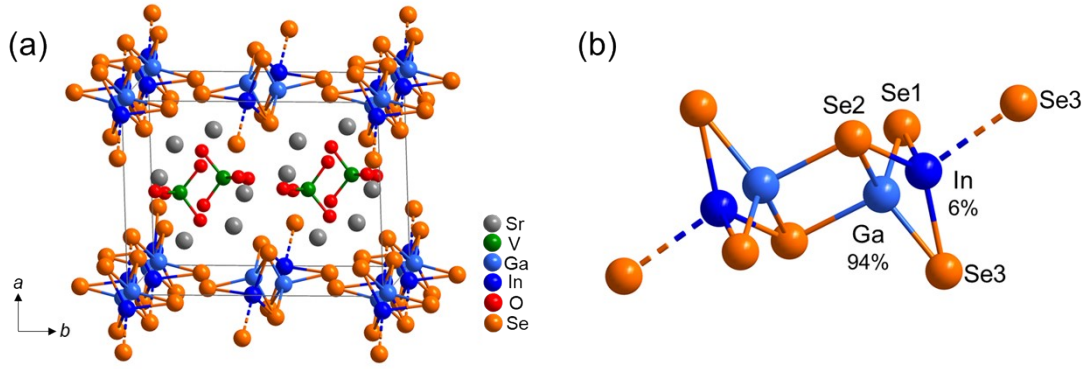

Figure S1. (a) Schematic crystal structure of $[Sr_3VO_4][Ga_{0.94}In_{0.06}Se_3]$. (b) Coordination environments of Ga and In atoms.

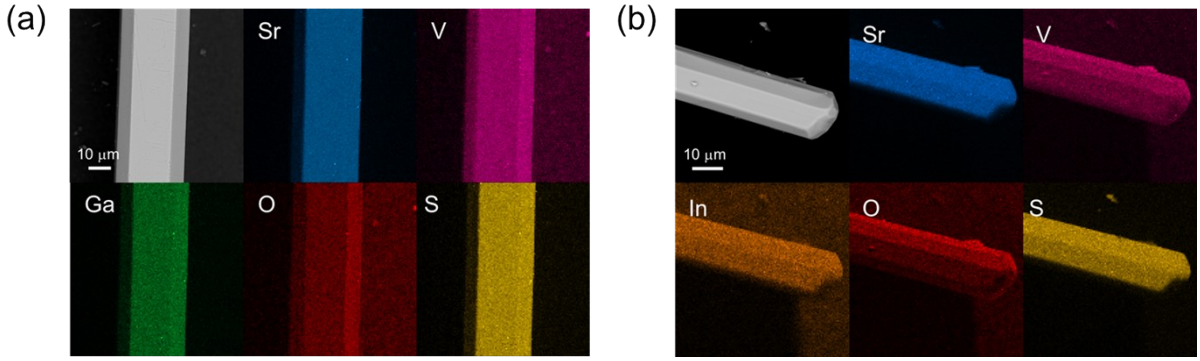

Figure S2. The SEM images and EDX mapping analysis of (a) $[Sr_3VO_4][GaS_3]$ and (b) $[Sr_3VO_4][InS_3]$ single crystals.

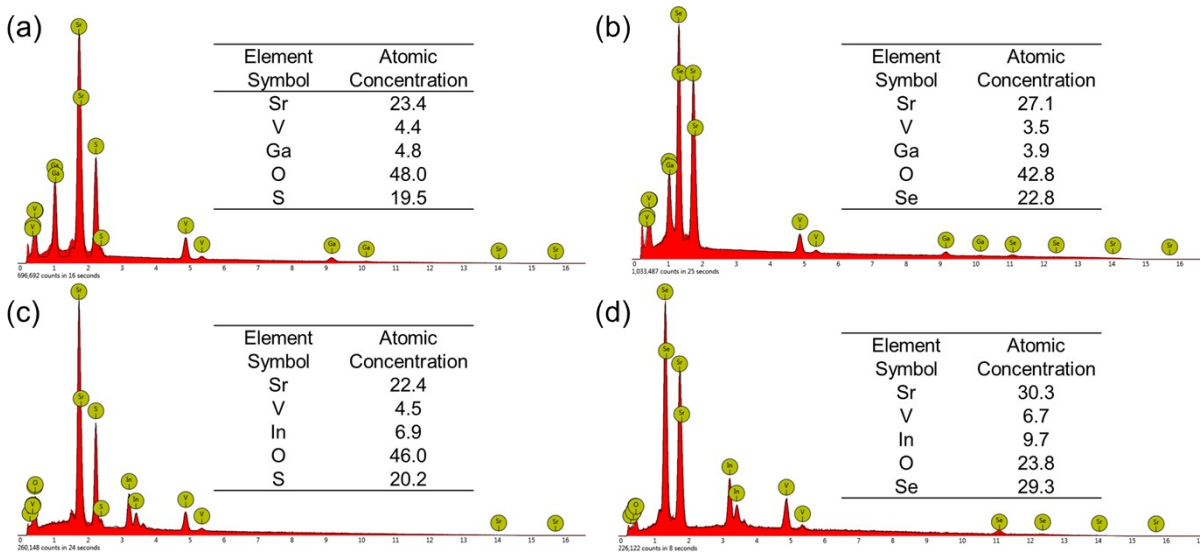

Figure S3. EDX spectra and element contents of (a) $[Sr_3VO_4][GaS_3]$, (b) $[Sr_3VO_4][GaSe_3]$, (c) $[Sr_3VO_4][InS_3]$ and $[Sr_3VO_4][InSe_3]$.

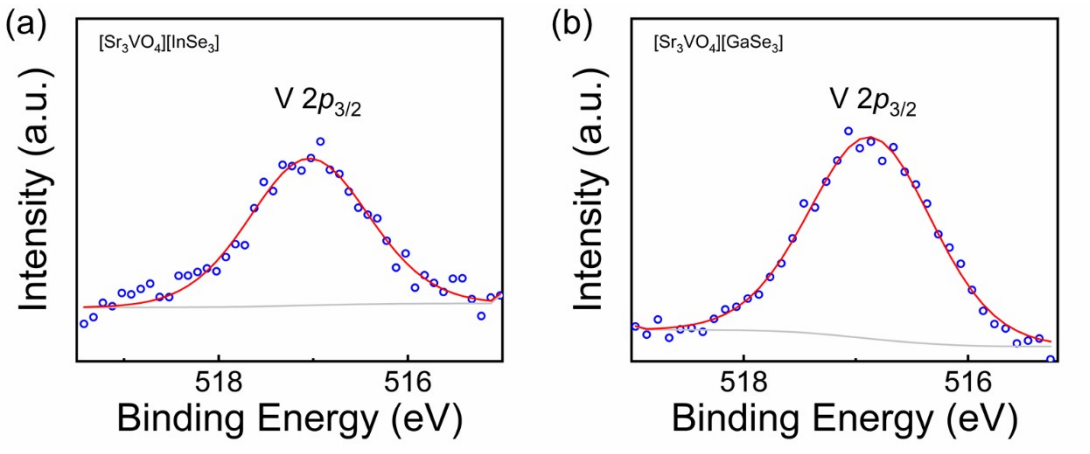

Figure S4. The high-resolution XPS spectra for V $2p_{3/2}$ core levels of (a) $[Sr_3VO_4][InSe_3]$ and (b) $[Sr_3VO_4][GaSe_3]$.

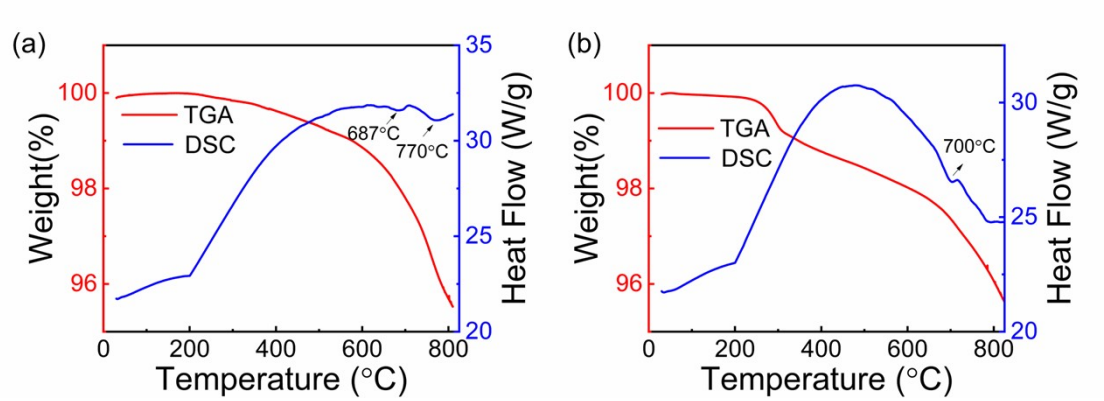

Figure S5. TGA-DSC curves of (a) $[Sr_3VO_4][InSe_3]$ and (b) $[Sr_3VO_4][GaSe_3]$.

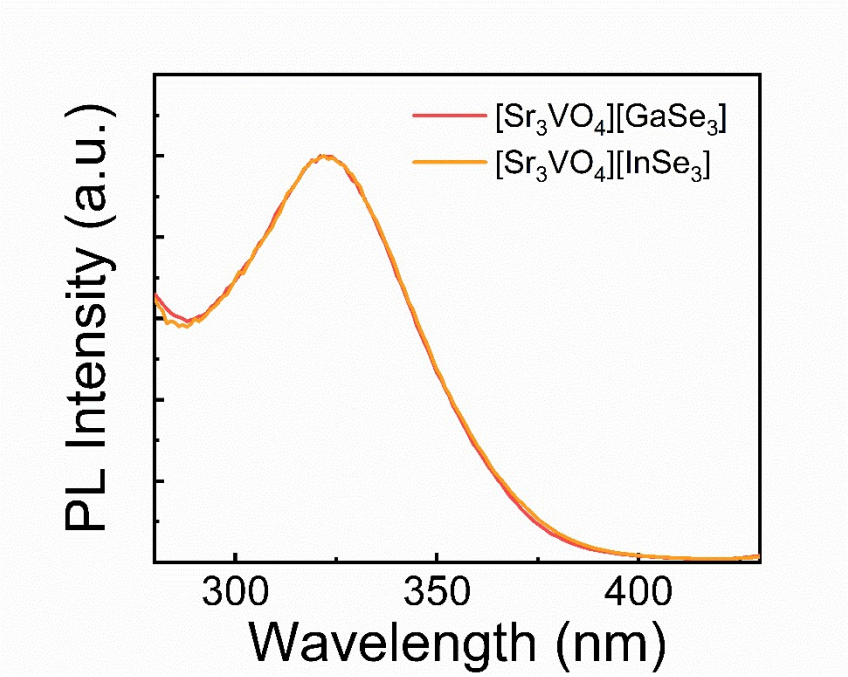

Figure S6. PL excitation spectra of the emissions at 455 nm.

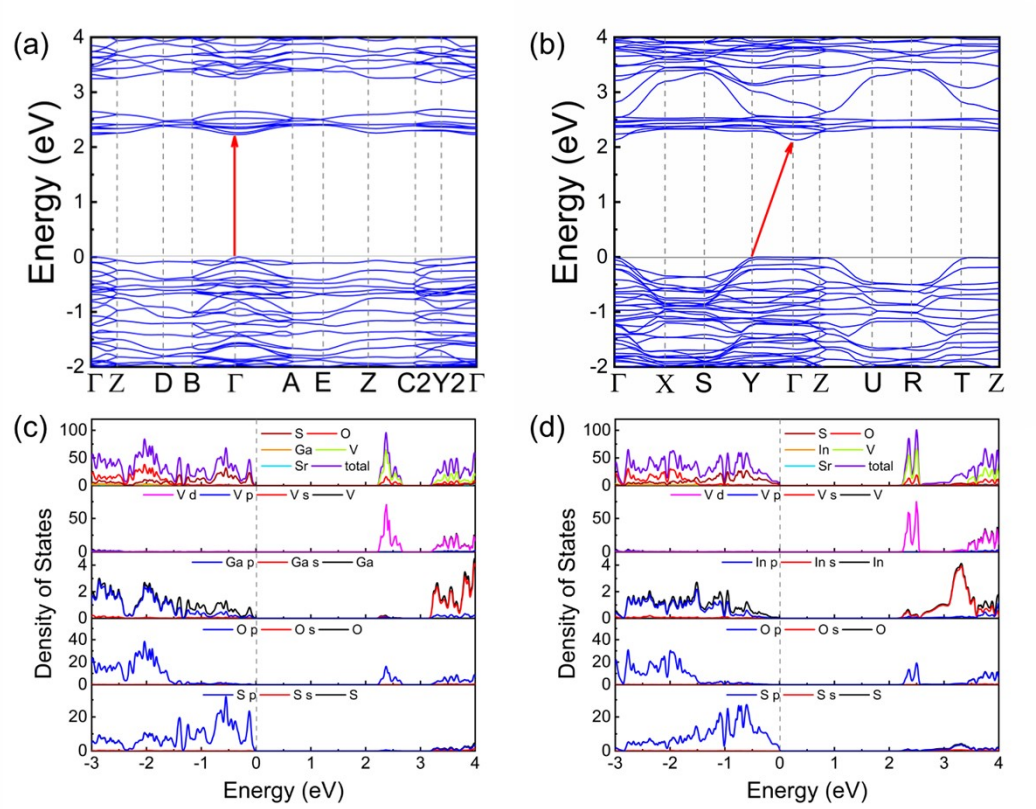

Figure S7. Band structures of (a) $[Sr_3VO_4][GaS_3]$ and (b) $[Sr_3VO_4][InS_3]$. Total and partial DOS of (c) $[Sr_3VO_4][GaS_3]$ and (d) $[Sr_3VO_4][InS_3]$.

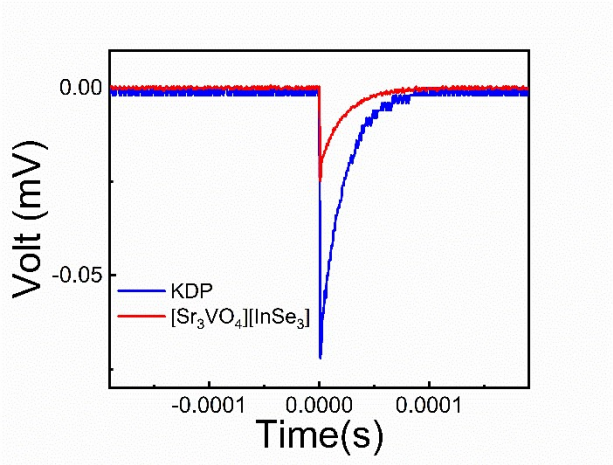

Figure S8. The SHG signals of $[Sr_3VO_4][InSe_3]$ and KDP in the size range of 150–212 μm.

2. Supplementary tables.

Table S1. Crystallographic data and the structure refinement of $[Sr_3VO_4][MQ_3]$ (M = Ga, In, Q = S, Se).

Formula	$[Sr_3VO_4][GaS_3]$	$[Sr_3VO_4][GaSe_3]$	$[Sr_3VO_4][InS_3]$	$[Sr_3VO_4][InSe_3]$
Space group	$P2_1/c$	$P2_1/c$	$Pmc2_1$	$Pmc2_1$
F_w(g·mol^{-1})	543.70	684.40	588.80	729.50
a (Å)	9.6119(3)	9.9155(3)	7.713(2)	7.8735(2)
b (Å)	13.3417(4)	13.0511(5)	9.765(2)	10.0396(3)
c (Å)	7.5036(2)	7.6839(3)	12.835(2)	12.9670(4)
V(Å^3)	950.84(5)	994.29(6)	966.8(2)	1025.00(5)
crystal color	white	yellow	white	yellow
ρ_c (g·cm^{-3})	3.798	4.572	4.045	4.727
μ (mm^{-1})	21.087	30.518	20.339	29.225
F(000)	992	1208	1064	1280
data/parameters	2332/109	2673/109	2127/131	2745/131
Flack parameter	-	-	0.397(7)	0.169(11)
R_{int}	0.0253	0.0240	0.0286	0.0366
$R1[I>2\sigma(I)]$	0.0152	0.0173	0.0218	0.0297
wR_2 (all data)	0.0332	0.0376	0.0489	0.0763
GOF	1.128	1.086	1.004	1.011

Table S2. Crystallographic data and the structure refinement of $[Sr_3VO_4][Ga_{0.62}In_{0.38}Se_3]$ and $[Sr_3VO_4][Ga_{0.94}In_{0.06}Se_3]$.

Formula	$[Sr_3VO_4][Ga_{0.62}In_{0.38}Se_3]$	$[Sr_3VO_4][Ga_{0.94}In_{0.06}Se_3]$
Space group	$Pmc2_1$	$P2_1/c$
F_w(g·mol^{-1})	701.43	686.99
a (Å)	7.8172(3)	9.9383(3)
b (Å)	9.9650(3)	13.0465(5)
c (Å)	12.9466(5)	7.6899(3)
V(Å^3)	1008.52(6)	997.02(6)
crystal color	yellow	yellow
ρ_c (g·cm^{-3})	4.620	4.577
μ (mm^{-1})	29.942	30.412
F(000)	1235	1212
data/parameters	2780/134	2505/119
Flack parameter	0.003(10)	-
R_{int}	0.0427	0.0223
$R1[I>2\sigma(I)]$	0.0238	0.0262
wR_2 (all data)	0.0526	0.0624
GOF	1.034	1.036

Table S3. Selected bond lengths (Å) and angles (°) of $[Sr_3VO_4][GaS_3]$ (Q = S, Se).

$[Sr_3VO_4][GaS_3]$		$[Sr_3VO_4][GaSe_3]$	
Ga–S1	2.3303(5)	Ga–Se1	2.3512(4)
Ga–S1	2.3486(5)	Ga–Se2	2.4469(4)
Ga–S2	2.2236(5)	Ga–Se2	2.5153(4)
Ga–S3	2.2145(5)	Ga–Se3	2.3583(3)
V–O1	1.716(2)	V–O1	1.712(2)
V–O2	1.701(2)	V–O2	1.717(2)
V–O3	1.717(2)	V–O3	1.718(2)
V–O4	1.722(2)	V–O4	1.732(2)
Sr1–O1	2.613(2)	Sr1–O1	2.760(2)
Sr1–O2	2.686(2)	Sr1–O4	2.499 (2)
Sr1–O2	2.695(2)	Sr1–O4	2.544(2)
Sr1–S1	3.090(5)	Sr1–Se2	3.2569(4)
Sr1–S2	2.8916(5)	Sr1–Se1	3.0443(3)
Sr1–S2	3.0171(5)	Sr1–Se1	3.1165(3)
Sr1–S3	3.1098(5)	Sr1–Se3	3.4005(3)
Sr2–O3	2.702(2)	Sr3–O3	2.659(2)
Sr2–O4	2.530(2)	Sr3–O2	2.552(2)
Sr2–O4	2.523(2)	Sr3–O2	2.612(2)
Sr2–S1	3.1436(5)	Sr3–Se2	3.3092(3)
Sr2–S2	3.0439(5)	Sr3–Se1	3.0074(3)
Sr2–S2	2.9284(5)	Sr3–Se1	3.0742(3)
Sr2–S3	3.1238(5)	Sr3–Se3	3.1665(3)
Sr3–O1	2.518(2)	Sr2–O1	2.575(2)
Sr3–O1	2.696(2)	Sr2–O1	2.645(2)
Sr3–O2	2.802(2)	Sr2–O2	2.646(2)
Sr3–O3	2.610(2)	Sr2–O3	2.598(2)
Sr3–O3	2.515(2)	Sr2–O3	2.663(2)
Sr3–O4	2.665(2)	Sr2–O4	2.590(2)
Sr3–S3	3.1024(5)	Sr2–Se3	3.2403(4)
S1-Ga-S1	95.87(2)	Se1-Ga-Se3	115.96(2)
S2-Ga-S1	111.44(2)	Se2-Ga-Se1	104.09(2)
S2-Ga-S1	105.59(2)	Se2-Ga-Se3	123.46(2)
S3-Ga-S1	114.89(2)	Se2-Ga-Se1	108.86(2)
S3-Ga-S1	107.94(2)	Se3-Ga-Se2	103.44(2)
S3-Ga-S2	118.79(2)	Se2-Ga-Se2	99.09(2)
O1-V-O2	107.87(7)	O1-V-O2	115.91(8)
O2-V-O3	115.57(7)	O1-V-O3	106.67(9)
O1-V-O3	106.16(7)	O2-V-O3	106.28(8)
O2-V-O4	107.23(7)	O1-V-O4	106.58(8)
O1-V-O4	114.53(7)	O2-V-O4	104.83(9)
O3-V-O4	105.72(7)	O3-V-O4	117.01(8)

Table S4. Selected bond lengths (Å) and angles (°) of $[Sr_3VO_4][InQ_3]$ (Q = S, Se).

$[Sr_3VO_4][InS_3]$		$[Sr_3VO_4][InSe_3]$	
In1–S3	2.462(3)	In1–Se1	2.569(2)
In1–S5	2.463(2)	In1–Se3	2.556(2)
In1–S4	2.481(2)	In1–Se4	2.594(2)
In2–S1	2.462(2)	In2–Se2	2.563(2)
In2–S2	2.465(3)	In2–Se4	2.593(2)
In2–S4	2.481(2)	In2–Se5	2.576(2)
V1–O1	1.735(8)	V1–O2	1.703(7)
V1–O3	1.723(7)	V1–O5	1.726(9)
V1–O5	1.704(6)	V1–O6	1.726(10)
V2–O2	1.732(8)	V2–O1	1.736(10)
V2–O4	1.703(6)	V2–O3	1.733(9)
V2–O6	1.716(7)	V2–O4	1.706(7)
Sr1–O1	2.555(7)	Sr1–O3	2.515(6)
Sr1–O5	2.612(5)	Sr1–O4	3.063(7)
Sr1–O4	2.621(6)	Sr1–O5	2.511(6)
Sr1–O3	2.631(7)	Sr1–Se1	3.276(2)
Sr1–S3	3.452(3)	Sr1–Se2	3.143(2)
Sr1–S4	3.341(2)	Sr1–Se3	3.113(2)
Sr2–O2	2.655(7)	Sr1–Se4	3.429(2)
Sr2–O4	2.600(5)	Sr1–Se5	3.240(2)
Sr2–O5	2.580(6)	Sr2–O1	2.625(9)
Sr2–O6	2.539(7)	Sr2–O2	2.683(7)
Sr2–S2	3.270(3)	Sr2–O3	2.563(10)
Sr3–O3	2.500(5)	Sr2–O4	2.658(7)
Sr3–O6	2.576(5)	Sr2–Se4	3.423(2)
Sr3–O4	2.830(5)	Sr2–Se5	3.413(2)
Sr3–S5	2.969(2)	Sr3–O2	2.638(7)
Sr3–S1	2.993(2)	Sr3–O4	2.651(7)
Sr3–S2	3.000(2)	Sr3–O5	2.678(9)
Sr3–S3	3.028(2)	Sr3–O6	2.549(9)
Sr4–O1	2.488(5)	Sr3–Se1	3.311(2)
Sr4–O2	2.489(5)	Sr4–O1	2.503(6)
Sr4–O5	3.095(6)	Sr4–O2	2.845(7)
Sr4–S1	2.994(2)	Sr4–O6	2.561(6)
Sr4–S5	3.032(2)	Sr4–Se1	3.111(2)
Sr4–S3	3.153(2)	Sr4–Se2	3.065(2)
Sr4–S2	3.187(2)	Sr4–Se3	3.083(2)
Sr4–S4	3.382(2)	Sr4–Se5	3.143(2)
S3-In1-S5	95.87(2)	Se3-In1-Se1	94.54(5)
S3-In1-S4	111.44(2)	Se3-In1-Se4	115.47(4)
S5-In1-S4	105.59(2)	Se1-In1-Se4	117.59(4)
S3-In1-S4	114.89(2)	Se3-In1-Se4	115.47(4)
S5-In1-S4	107.94(2)	Se1-In1-Se4	117.58(4)
S4-In1-S4	118.79(2)	Se4-In1-Se4	97.64(5)
S1-In2-S2	93.97(7)	Se2-In2-Se5	93.56(5)
S1-In2-S4	115.92(5)	Se2-In2-Se4	113.53(4)

S2-In2-S4	115.25(6)	Se5-In2-Se4	118.62(4)
S4-In2-S4	101.45(8)	Se4-In2-Se4	99.89(5)
O5-V1-O5	107.1(4)	O2-V1-O2	107.9(5)
O5-V1-O3	113.0(2)	O2-V1-O6	107.6(3)
O5-V1-O1	109.1(2)	O2-V1-O5	113.9(3)
O3-V1-O1	105.4(4)	O6-V1-O5	105.7(5)
O4-V2-O4	107.4(4)	O4-V2-O4	108.9(5)
O4-V2-O6	107.2(2)	O4-V2-O3	109.1(3)
O4-V2-O2	114.2(2)	O4-V2-O1	112.8(3)
O6-V2-O2	106.3(3)	O3-V2-O1	103.9(5)

Table S5. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) of $[Sr_3VO_4][GaS_3]$.

Label	x	y	z	Occupancy	U_{eq}*
Sr1	0.31345(2)	0.34022(2)	1.03060(2)	1	0.00736(5)
Sr2	0.71361(2)	0.18926(2)	0.99112(2)	1	0.00670(5)
Sr3	-0.00289(2)	0.43274(2)	1.25439(2)	1	0.00598(5)
Ga1	0.44907(2)	0.45739(2)	0.67366(3)	1	0.00632(6)
V1	0.01382(3)	0.32005(2)	0.76074(4)	1	0.00398(7)
S1	0.33812(5)	0.47145(4)	1.37324(6)	1	0.0076(2)
S2	0.49820(5)	0.29859(4)	0.74833(6)	1	0.0064(2)
S3	0.32718(5)	0.54732(4)	0.84393(7)	1	0.0085(2)
O1	0.05241(2)	0.39851(2)	0.94282(2)	1	0.0073(3)
O2	0.1551(2)	0.2439(2)	0.7556(2)	1	0.0087(3)
O3	-0.0298(2)	0.3961 (2)	0.5760(2)	1	0.0074(3)
O4	-0.1302(2)	0.2440(2)	0.7666(2)	1	0.0077(3)

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S6. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) of $[Sr_3VO_4][GaSe_3]$.

Label	x	y	z	Occupancy	U_{eq}*
Sr1	0.22797(2)	0.20006(2)	0.97968(3)	1	0.00685(6)
Sr2	0.51394(2)	0.44229(2)	0.75290(3)	1	0.00651(5)
Sr3	0.79238(2)	0.17691(2)	0.54355(3)	1	0.00709(6)
Se1	1.00119(2)	0.28949(2)	0.75653(3)	1	0.00605(6)
Se2	1.16761(2)	0.53389(2)	0.60399(3)	1	0.00731(6)
Se3	0.79808(2)	0.54405(2)	0.87357(3)	1	0.00790(6)
Ga1	0.95049(3)	0.46081(2)	0.68738(3)	1	0.00752(6)
V1	0.51070(4)	0.30934(3)	0.26019(5)	1	0.00367(8)
O1	0.47832(17)	0.38755(13)	0.4337(2)	1	0.0065(3)
O2	0.64968(17)	0.23158(13)	0.2811(2)	1	0.0066(3)
O3	0.54072(17)	0.38808(13)	0.0857(2)	1	0.0072(3)
O4	0.37544(17)	0.22593(13)	0.2420(2)	1	0.0062(3)

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S7. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) of $[Sr_3VO_4][InS_3]$.

Label	x	y	z	Occupancy	U_{eq}*
Sr1	1	-0.04325(9)	0.63452(7)	1	0.0077(2)
Sr2	0.5	-0.0223(2)	0.75374(7)	1	0.0087(2)
Sr3	0.7495(2)	0.27908(7)	0.51383(5)	1	0.0072(2)
Sr4	0.7510(2)	0.29261(7)	0.88934(5)	1	0.0082(2)
V1	1	0.0043(2)	0.8833(2)	1	0.0045(3)
V2	0.5	-0.0007(2)	1.0052(2)	1	0.0047(4)
In1	1	0.55060(7)	0.72343(6)	1	0.0067(2)
In2	0.5	0.55107(7)	0.72632(6)	1	0.0064(2)
S1	0.5	0.5236(2)	0.9170(2)	1	0.0069(5)
S2	0.5	0.3027(3)	0.6923(2)	1	0.0066(6)
S3	1	0.3013(3)	0.6947(2)	1	0.0074(7)
S4	0.7490(2)	0.6789(2)	0.6520(2)	1	0.0099(3)
S5	1	0.5305(2)	0.9147(2)	1	0.0063(5)
O1	1	0.1552(7)	0.9546(6)	1	0.008(2)
O2	0.5	0.1378(8)	0.9209(5)	1	0.009 (2)
O3	1	-0.1252(8)	0.9745(5)	1	0.008(2)
O4	0.3220(7)	-0.0100(6)	1.0834(4)	1	0.009(2)
O5	0.8223(8)	0.0014(6)	0.8044(4)	1	0.010 (2)
O6	0.5	-0.1445(7)	0.9284(5)	1	0.007(2)

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S8. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) of $[Sr_3VO_4][InSe_3]$.

Label	x	y	z	Occupancy	U_{eq}*
In1	1	-0.04785(8)	0.58998(7)	1	0.0070(2)
In2	0.5	-0.04895(9)	0.59424(7)	1	0.0078(2)
Sr1	0.2509(2)	0.21757(9)	0.42727(8)	1	0.0075(2)
Sr2	0.5	0.4650(2)	0.1867(2)	1	0.0066(2)
Sr3	0	0.5230(2)	0.5665(5)	1	0.0074(3)
Sr4	0.2494(2)	0.76925(9)	0.31342(8)	1	0.0068(2)
Se1	1	0.2031(2)	0.62853(8)	1	0.0066(3)
Se2	0.5	-0.0240(2)	0.3975(2)	1	0.0075(2)
Se3	1	-0.0182(2)	0.3942(2)	1	0.0072(2)
Se4	0.75205(9)	-0.1887(2)	0.66381(9)	1	0.0093(2)
Se5	0.5	0.2044(2)	0.62589(8)	1	0.0067(3)
V1	1	0.5015(2)	0.3152(2)	1	0.0045(4)
V2	0.5	0.4945(3)	0.4382(2)	1	0.0043(4)
O1	0.5	0.623(2)	0.3482(7)	1	0.010(2)
O2	0.8252(9)	0.5096(7)	0.2382(5)	1	0.009(2)
O3	0.5	0.3512(8)	0.3637(7)	1	0.006(2)
O4	0.6762(9)	0.4952(7)	0.5147(5)	1	0.010(2)
O5	1	0.3675(9)	0.3987(7)	1	0.007(2)
O6	1	0.6414(9)	0.3926(7)	1	0.009(2)

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.