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Chemical Perspectives of Heteroanionic Compounds and their Applications for Superconductors, Photoluminescent response, Nonlinear optical materials, and Thermoelectrics

Karishma Prasad [#], Vivian Nguyen [#], Bingheng Ji [#] , Jasmine Quah , Danielle Goodwin , Jian Wang [*]

Department of Chemistry and Biochemistry, Wichita State University, Wichita, Kansas 67260, United States

# Equally contributed

Corresponding author: Jian Wang jian.wang@wichita.edu

Table S1. Selected heteroanionic compounds synthesized by hydrothermal/solvothermal reactions

Compounds	Synthetic conditions	Products	Ref
$[O_2Pb_3]_2(BO_3)I$	PbI_2 (0.52 mmol, 0.240 g), $LiBO_2$ (5.23 mmol, 0.260 g), and distilled water (6 mL) was sealed in an autoclave equipped with teflon liner (23 mL). The autoclave was heated to 220 °C for 72 h	Crystal size-- 0.177 mm × 0.160 mm × 0.054 mm	[1]
$Li_4(B_7O_{12})Cl$	Heating B_2O_3/Li_2Omixtures in molar ratios at about 900K in an excess of fused LiCl or LiBr.	polycrystalline powder	[2]
$K_2Bi_2(SeO_3)_3F$	$KF\cdot 2H_2O$ (2 mmol, 188 mg), SeO_2 (2 mmol, 222 mg), Bi_2O_3 (0.4 mmol, 187 mg) and 40.0 % solution of HF (25 µL) were put together with 2 mL H_2O. then sealed in autoclave equipped with a Teflon liner and gradually heated to 270C, held for 66 hours.	polycrystalline powder	[3]
$Bi_3(SeO_3)_3(Se_2O_5)F$	Bi_2O_3(4.00×10−4mol ,0.186 g) and SeO_2 (1.60×10−3mol ,0.178 g) loaded in a 23 mL Teflon cup.0.1mL of HF (50%, aq) solution added to the mixture. The Teflon cup loaded in an autoclave. The autoclave was heated to 230°C at a rate of 1°C min−1, dwelled at the temperature for 72 h, and cooled to room temperature at a rate of 0.1°C min−1.	Crystal size-- (0.034 mm × 0.141 mm × 0.449 mm)	[4]
$Rb_3SbF_3(NO_3)_3$	SbF_3 (1.00 mmol, 0.179 g), $RbNO_3$ (4.00 mmol ,0.588 g) were added into 5 mL of deionized water with a few drops of concentrated nitrate acid inhibiting the hydrolysis of SbF_3, and the mixture was stirred for 20 minutes while heating at 80 °C.	polycrystalline powder	[5]

Table S2. Selected heteroanionic compounds synthesized by high temperature flux methods.

Compounds	Synthetic conditions	Products	Ref
$Zn_6S_5Cl_2$	$ZnCl_2$ (1 mmol, 136 mg), Zn (5 mmol, 325 mg) and S (5 mmol, 160 mg) the tube was heated to 500 1C in 12 h	polycrystalline powder	[6]
$Eu_2B_5O_9S$	Eu_2O_3, S, B, and B_2O_3, KI as the flux. The tube heated from room temperature to 1223 K at the speed of 60 K/h, homogenized for 10 days, and finally cooled to 573 K in 5days with the furnace powered off.	polycrystalline powder	[7]
$Zn_4B_6O_{12}S$	ZnO, B_2O_3, S, and B were mixed in a molar ratio of 12:8:3:2, KI as flux. The quartz tube was heated to 950 °C in 25 h	polycrystalline powder	[8]
GdFeAsO	As and Gd mixed with NaI/KI.the ampoules were slowly heated to 1320 K within 24 h. An annealing period of three to six days was applied, followed by slow cooling to 870 K with 1 K/h	polycrystalline powder	[9]
Zn_2NX (X = Cl, Br)	Zn_3N_2 and $ZnCl_2$ were evenly mixed with a 1:2 molar ratio. The excess of zinc halide as a flux, the mixture was heated to 600 °C within 24 h,	polycrystalline powder	[10]

Table S3. Selected heteroanionic compounds synthesized by high temperature solid state methods

Compounds	Synthetic conditions	Products	Ref
$Pb_8B_9O_{21}F$	PbO (0.0375 mol, 8.37 g), PbF_2 (0.0025 mol 0.613 g,) and H_3BO_3 (0.045 mol ,2.78 g,) in air. Then the reaction mixture was elevated to 500 °C and sintered at this temperature for 48 h .	polycrystalline powder	[11]
$Cs_3B_3O_3F_6$	$CsBF_4$ (3 mmol, 0.370 g), CsF (6 mmol, 0.908 g), and H_3BO_3 (6 mmol, 0.722 g) for $Cs_3B_3O_3F_6$, heated to 350 °C and held at this temperature in air for 10 h.	Crystal size- ($1\times1\times0.5\ mm^3$)	[12]
BaTi2Bi2O or $(SrF)_2Ti_2Bi_2O$	BaO, SrF_2, SrO, Ti, Bi heated for 50 h at 850C for $BaTi_2Bi_2O$ and at 900C for $(SrF)_2Ti_2Bi_2O$, followed by controlled cooling at a rate of 25C/h to room temperature	polycrystalline powder	[13]
$SrZnSO:Bi^{3+}$	$SrCO_3$, ZnS, Bi_2O_3 and H_3BO_3 here, H_3BO_3 acts as a fluxing agent to lower the sintering temperature, sintered at 1050 °C for 9 h	polycrystalline powder	[14]
$Ba_2Ti_2Cr_2As_4O$	Ba, Ti, As, Cr and TiO_2, heated to 1253 K in an evacuated quartz tube, holding for 1500 min.	polycrystalline powder	[15]

Table S4. Selected Oxohalides with structural information and physical properties.

Formula	Space Group	Structure Type	Structure Units	Properties	Ref
Li(SO_3F)	$C2/m$		[LiO_4] [SO_3F]		16
$LiNaCoPO_4F$	$P2_1/c$	$LaNaNiPO_4F$	[CoO_4F_2] [PO_4]	Eg(cal)=4.5 V	17
$BaZnBe_2(BO_3)_2F_2$	P -3		[BaO_6F_6] [ZnO_6]	Eg(cal) = 4.55 eV Δn = 0.063 at 1064 nm	18
$Pb_2(V_2O_4F)(VO_2)(SeO_3)_3$	$P\ 2_12_12_1$		[VO_5F] [VO_6] [VO_5] [SeO_3]	SHG: 0.3 × (KDP), Eg(exp)= 2.35 eV LDT= 61 × $AgGaS_2$	19
$KYb(SO_4)F_2$	$P2_1/m$		[YbO_4F_4]	Eg(exp)= 5.36eV, paramagnetic behavior down to 2 K with a dominant antiferromagnetic coupling between spin carriers.	20
$(Ba_3F)(Ta_4O_{12}F)$	$P4_2/mnm$		[TaO_6] [TaO_5F]		21
$Na_3Fe_2(PO_4)_2F_3$	$P4_2/mnm$	$Na_3V_2(PO_4)_2F_3$	[PO_4] [FeO_4F_2]	Reasonable achievable capacity and stable cycle life for Li- ion batteries with poor Na-ion capacity	22
α-$Ba_3Zn_2(BO_3)_3F$	$P2_1/c$	Bi_2MoO_6	[ZnO_2O_2BO]$_2$ [$Zn_2O_5O_2BO$][BO_3]		23
$(ClOF_2)(NbF_6)$	$Pna2_1$	$(ClOF_2)(AsF_6)$	$[ClOF_2]^+$ $[NbF_6]^-$		24
$Mg_7Ge_2O_{10}F_2$	$Pbam$		[MgO_4F_2] [GeO_4]		25
$Lu_3F(SeO_3)_4$	$P6_3$		[SeO_3] [LuO_7F[	SHG:2.5 × KDP, Eg(exp)=3.57 eV, LDT: 36 × $AgGaS_2$	26
$KMoO_2F_3$	$P2_12_12_1$		[MoO_2F_4]		27
$CsSiP_2O_7F$	$P2_1$		[$SiP_2O_{10}F$] made by [SiO_5F] and [P_2O_7]	SHG: 0.7 × KDP, Eg(cal) =6.4 eV	28
$Li_3CaB_2O_5F$	$Pnma$		[B_2O_5] [LiO_4F] [LiO_2F_3]		29
$KLa(PO_2F_2)_4$	$P2_1/c$		$[KO_6F_4]^{15-}$ $[PO_2F_2]^-$ $[LaO_8]^{13-}$	Eg(cal) =5.87 eV, Δn = 0.023 at 1064 nm	30
$Bi_3(SeO_3)_3(Se_2O_5)F$	$P2_1$		[BiO_7], BiO_6F] [SeO_3] [Se_2O_5]	SHG: 8 × KDP, Eg(exp)=3.8 eV	4
$CsGa_3F_6(SeO_3)_2$	$P6_3mc$		[GaO_2F_4] [SeO_3]	SHG: 5.4 × KDP, Eg(exp)=3.65 eV	31
$RbGa_3F_6(SeO_3)_2$	$P6_3mc$		[GaO_2F_4] [SeO_3]	SHG: 5.6 × KDP, Eg(exp)=3.57 eV	31
$K_4(PO_2F_2)_2(S_2O_7)$	$C2/c$		$[S_2O_7]^{2-}$ $[PO_2F_2]^-$	Eg(cal) =5.193 eV, Δn = 0.015 at 1064 nm	32
$Ba(MoO_2F)_2(SeO_3)_2$	$Aba2$		[MoO_5F] [SeO_3]	SHG: 2.8 ×KDP,	33,3

				Eg(exp)=3.23 eV, Eg(cal)=2.52 eV	4
α-$Na_2Fe(PO_4)F$	$P2_1/c$	$Na_2Zr(SiO_4)O$	$[NaO_4F_2]$ $[PO_4]$	ca. 90 mAh g^{-1}	35
$CsZn_2(BO_3)F_2$	$R32H$		$[BO_3]$ $[ZnO_3F]$	Eg(exp)=6.2 eV, SHG: 3.2×KDP	36
$K_2Sb(P_2O_7)F$	$P4bm$		$[P_2O_7]$ $[SbO_4F]$	Δn = 0.157 at 546 nm, SHG: 4.0× KDP, Eg(exp)=4.74 eV	37
$Li_5VF_4(SO_4)2$	$P2_1/c$		$[V^{3+}F_2O_4]$ $[SO_4]$	high ionic conductivity of 2.2 × 10^{-2} mS cm^{-1}	38
$Li(W_2O_2F_9)$	$Pbcn$		$[W_2O_2F_9]^{-}$		39
$Pb_2Al_3F_3(Te_6F_2O_{16})$	$P4/mbm$		$[Te_6F_2O_{16}]^{10-}$ $[AlO_4F_2]$	Eg(exp)=4.1 eV, Eg(cal)=2.13 eV	40
$FeNd_2(SeO_3)_4Cl$	$C2/c$		$[NdO_{10}]$ $[SeO_3]$ $[FeO_4Cl]$	Possible “hidden antiferromagnetic ordering behavior”.	41
K_2SnOF_4	$Pnma$		$[SnO_2F_4]^{4-}$		42
$K_2WO_3F_2$	$Pnma$		$[WO_4F_2]^{4-}$		42
$K_5Sn_2OF_{11}$	$Ama2$		$[Sn_2OF_{10}]^{4-}$		43
$RbBi(SeO_3)F_2$	$P\ n\ m\ a$		$[BiO_3F_4]$ $[SeO_3]$	Eg(exp)=4.01eV	44
$Na_3Cs(MoO_2F_4)_2$	$P2_1/c$		$[MoO_2F_4]^{2-}$ $[NaF_6]^{5-}$ $[NaOF_7]^{8-}$ $[IO_3]^{-}$, $[MoO_4]^{2-}$	Eg(cal)=2.7 eV, Δn = 0.210 at 1064 nm	45
$Cs_3B_3O_3F_6$	$Pbcn$		$[B_3O_3F_6]$ $[BO_2F_2]$	Δn=0.0069 at 532 nm), Eg(cal)=5.772 eV	12
$K_2Bi_2(SeO_3)_3F_2$	Cm		$[Bi(1)O_6F_2]$ $[Bi(2)O_5F_2]$ $[SeO_3]$	Eg(exp)=3.72 eV, LDT= 81.3 (1) $AgGaS_2$, Δn = 0.105(1) at 546.1 nm, KDP: 15× KDP	3
$Rb_2Bi_2(SeO_3)_3F_2$	Cm		$[Bi(1)O_6F_2]$ $[Bi(2)O_5F_2]$ $[SeO_3]$	Eg(exp)=3.73 eV, LDTs=48.8 (2) × $AgGaS_2$, Δn = 0.088(2) at 546.1 nm, SHG: 14.4×KDP	3
$Al_8(BO_3)_4(B_2O_5)F_8$	$P4_2/nmc$		$[AlO_4F_2]$ $[BO_3]$ $[B_2O_5]$	Eg(cal)= 5.74 eV	46
$PbB_5O_7F_3$	$Cmc2_1$	$CaB_5O_7F_3$	$[BO_3]$ $[BO_3F]$ $[PbO_6F_3]$	SHG: 6 × KDP, Δn = 0.12 at 1064 nm	47
$La_3F_2Se_2TaO_4$	$Pnma$	$La_3NbSe_2O_4F_2$	$[TaO_5Se]^{7-}$		48
$(XeF_5)_2(CrF_6)(CrOF_4)_2$	P-1		$[XeF_5]^{+}$ $[Xe_2F_{11}]^{+}$ $[CrOF_5]^{2-}$ $[Cr_2O_8F_5]^{2-}$		49
$K(Mo_2O_2F_9)$	$P2/c$		$[Mo_2O_2F_9]^{-}$		50
$Rb_3SbF_3(NO_3)_3$	$P2_1$		$[SbF_3(NO_3)_3]^{3-}$	SHG: 2.2 × KDP, Eg(exp)= 3.75 eV, Eg(cal)= 3.08 eV	5

$Cs_8Dy_2Ge_{16}O_{38}F_2$	*Pnn*2		$[Ge_2O_7F]$		51
$CsB(PO_4)F$	$P2_13$	K_3VO_4(cP32)	$[PO_4]$ $[BO_3F]$	SHG: 0.3 × KDP,	52
$KYb_2F_5(SO_4)$	*Pbcm*	$LaV_2O_6IO_3$	$[YbO_2F_6]$ $[SO_4]$	weak magnetic interaction between the neighboring Yb^{3+} ions	53
$RbBi_2(SeO_3)F_5$	*P*-1		$[BiO_3F_5]$ $[SeO_3]$	Eg(exp)= 4.18eV	54
$Pb_3B_6O_{11}F_2$	$P2_1$	$Ba_3B_6O_{11}F_2$	$[Pb_3O_xF_2$ (x = 4, 5, 6)], $[FPb_3]$ layer, $[BO_4]$ $[BO_3]$	Eg(exp)= 3.02eV, Eg(cal)= 2.55 eV, d Δn = 0.071 at 534 nm , SHG: ~4 × KDP	55
PbB_5O_8F	*Pbca*		$[B_5O_{10}F]^{6-}$	Δn = 0.0685 at 1064 nm, Δn = 0.0737 at 400 nm	56
$PbB_2O_3F_2$	$P3_1m$		$[BO_3F]$	SHG:13 × KDP	57
$SnB_2O_3F_2$	$P3_1m$		$[BO_3F]$	SHG:4 × KDP	58
$Pb_8(B_9O_{21})F$	*R*-3*cH*		$[B_9O_{21}]^{15-}$ $[BO_3]$	cutoff edge is about 276 nm	11
Pb_2BO_3F	$P6_3/m$		$[PbO_3F_2]$ $[BO_3]$	melts congruently at 448 °C	59
$Pb_3O(BO_3)F$	*Pbcm*		$[PbO_3F]$ $[PbO_4]$ $[BO_3]$		60

Table S5. Selected Oxysulfides and Oxyselenides with structural information and physical properties.

Formula	Space Group	Structure type	BBU's	Property	Ref
BiAgOSe	*P4/nmmZ*	$CuHfSi_2$	$[Bi_2O_2]^{2+}$ $[Ag_2Se_2]^{2-}$	E(g)= 0.95 eV. lower lattice thermal conductivities (0.61 $W{\cdot}m^{-1}{\cdot}K^{-1}$ at room temperature and 0.35 $W{\cdot}m^{-1}{\cdot}K^{-1}$ at 650 K	61
$A_2Mn(SeO_4)F_3$ (A = K, Rb, Cs)	*Pbcn*		$_\infty[MnF_3O_2]^{4-}$ $[SeO_4]$		62
$Ti_4O(Se_2)_4Br_6$	*P*121/*c*1		$[Ti_4(\mu_4\text{-}O)]$ $[Se_2]^{2-}$	Raman band at 224 cm^{-1}	63
$Sr_{3-x}Ca_xFe_2O_5Cu_2Ch_2$ (Ch= S, Se; x=1, 2)	*I4/mmm*		$[FeO_5][Cu_2Ch_2]$		64
$RETa_2MgQB_8O_{26}$ (RE = Sm, Eu, Gd; Q = S, Se), $Eu_6Ta_2MgSB_8O_{26}$ (1) $Sm_6Ta_2MgSeB_8O_{26}$ (2) $Eu_6Ta_2MgSeB_8O_{26}$ (3), $Gd_6Ta_2MgSeB_8O_{26}$ (4)	*P*-3		$[B_4O_{10}]^{8-}$ $_\infty[Mg(TaB_4O_{13})_2]^{16-}$	E(g)= 3.62, 3.73, 3.56, and 3.79 eV (1−4)	65
$A_2F_2Fe_2OQ_2$ (A=Sr, Ba; Q=S, Se)	*I4/mmm*	$Fe_2La_2O_3Se_2$	$[Sr_2F_2]$ $[Sr_nSe_{n+2}]$	magnetic semiconductors that undergo a long-range antiferromagnetic ordering below 83.6-106.2 K	66
$YSeBO_2$	*Cmc*21		$[BO_3]^{3-}$ $[YO_3Se_4]^{11-}$	E(g)= 3.45 eV	67
$LnCrSe_2O$ (Ln = Ce−Nd)	*C*12/*m*1	$AgBi_3S_4Br_2$	$[Cr1Se6]^{9-}$ $[Cr_2Se_4O_2]^{9-}$	$LnCrSe_2O$ (Ln = Ce−Nd) show antiferromagnetic ordering with T_N = 125, 120, and 118 K, respectively. Heat capacity measurement for $NdCrSe_2O$ indicates that the Debye temperature is 278.4 K.	68
$Ba_2NiO_2Ag_2Se_2$	*I4/mmm*		$[NiO_2]$ $[Ag_2Se_2]$	G type spin order at 130 K.	69

Table S6. Selected oxypnictides with structural information and physical properties.

Formula	Space Group	BBU's	Properties	Ref
$Cu_2(PO_4)F$	*C2/c*	Cu coordinated by four O and two F		[70]
$Te_2Se_8(AsF_6)\cdot SO_2$	$P2_1/c$	$[Te_2Se_8]^{2+}$ bicyclic cluster formed by six-membered ring fused with 8-membered ring.		[71,72]
$Cu_2(AsO_4)Cl$	$P2_1/m$	Face sharing Cu-containing octahedra create infinite zigzag chains and corner sharing with As tetrahedra		[73]
Eu_4As_2O	*I4/mmm*	La_2Sb type with O atoms occupying octahedral holes, closely related to K_2NiF_4 structure		[74]
$LaFeAsO_{1-x}F_x$	*Cmma* *P4/nmm*	Stacked $[FeAs_4]$ layers and $[La_4O]$ layers F-doped on O sites	ion carrier / superconductivity	[75–78]
$Pb_5(AsO_4)_3Cl$	$P2_1$ $P2_1/b$ $P6_3/m$	$[AsO_4]$ tetrahedra	monoclinic to hexagonal transformation through temperature	[79–84]
PrFeAsO	*P4/nmm*	Pr polyhedra, Fe polyhedra, As polyhedra, O tetrahedra		[85,86]
$(SrF)_2Ti_2As_2O$	*I4/mmm*	$[Ti_2O]$ square planar layer alternating with $[Sr_2F_2]$	resistivity and susceptibility, thermoeletric power, CDW/SDW	[87]
LaNiOAs	*P4/mmm*	Alternating [La-O] and [Ni-As] layers	superconductor. Pauli paramagnetism	[88]
GdFeAsO	*P4/nmm* *Cmme*	Alternating [As-Fe] and [Gd-O] layers	Structural transition magnetic transition	[9,86]
$Ce_9Au_{4.91}As_8O_6$	*Pnnm*	$[Au_5As_8]$, $[Ce_4O_3]_2$		[89]
$SrOCuSbS_2$	$P2_1/m$	Infinite $[Cu_2S_6]$ chain linked $[SbS_4O]$ layers separated by Sr	photoelectric properties	[90]
$Sr_2Mn_3Sb_2O_2$	*I4/mmm*	$[Mn_2Sb_2]$ and $[MnO_2]$ layers separated by Sr cation	magnetic properties	[91]
$Sm_9Sb_5O_5$	*P4/n*	Double layer [SmSb] and $[SmO_4]$ tetrahedra		[92]
$Ho_8Sb_3O_8$	*C2/m*	$[Ho_4O]$ edge sharing tetrahedra	electrical properties	[93]
$Eu_5Cd_2Sb_5O$	*Cmcm*	$[CdSb_4]$ tetrahedra corner sharing, forming pentagonal channels		[94]
$PbSbO_2Br$	*I4/mmm*	$[O\text{-}Pb/Sb_4]$ tetrahedra	Eg(cal)= 2.67 eV	[95]
$Bi_2(BiPb)WO_8Cl$	*P4*	$[Bi_2O_2]$ layers $[WO_6]$ octahedra $[PbO_4]$ tetrahedra		[96]
BiCuOSe	*P4/nmm*	$[Bi_2O_2]$ layers $[Cu_2Se_2]$ layers		[97–100]

Ca_4P_2O	*I4/mmm*	P surrounded by nine Ca atoms (tetragonal antiprism distorted) O atoms fill octahedral holes		101,102
UCuPO	*P4/nmm*	[U_2O_2] and [Cu_2P_2] layers	electrical resistivity magnetic susceptibility	103–105
LaNiOP	*P4/nmm*	Alternating stack [La-O] and [Ni-P] tetrahedra	Superconducting ~3K	106,107
ROTPn (R = La, Nd, Sm, Gd; T = Mn, Fe, Co, Ni, Cu; Pn = P, As, Sb)	*P4/nmm*	[TPn] and [RO] layers	superconducting	108–110
REZnPO (RE=Y, La-Nd, Sm, Gd, Dy, Ho)	*R*-3*m* *P4/nmm*	Alternate stacks of [RE-O] and [Zn-P]	magnetic, electronic, and optical properties	111
LnRuPO (Ln=La-Nd, Sm, Gd)	*P4/nmm*	Ln coordinated by four P and four O making square antiprism, [RuP_4] tetrahedra		112
$Sr_2CrO_2Cr_2As_2$	*I4/mmm*	[CrO_2] sheets, [CrAs] layers	magnetic properties	113,114
$Sr_2CrO_2Cr_2OAs_2$	*P4/mmm*	[CrO_4As_2] and [CrO_2As_4] octahedra, [Sr_2CrO_3] layers	magnetic properties	115
Sr_2M_3As2O2 (M_3=Mn_3, Mn_2Cu, $MnZn_2$)	*I4/mmm*	[CuO_2] and [Cu/Mn-As] layers	magnetic and electronic properties	116
Sr_2CrO_3FeAs	*P4/nmm*	[FeAs] layers, perovskite-like [Sr_2CrO_3] block	magnetic and electronic properties	117
Ba_2CrO_3FeAs	*P4/nmm*	[FeAs] layers, perovskite-like [Ba_2CrO_3] block	magnetic and electronic properties	117
$A_2MnZn_2As_2O_2$ (A=Sr, Ba)	*I4/mmm* *P4/nmm*	Square planar [MnO_2] [Zn_2As_2] layers	magnetic	118
$Ba_2Ti_2Cr_2As_4O$	*I4/mmm*	[Ti_2As_2O] and [Cr_2As_2] layers	magnetic properties AFM phase transition	15
$Ba_2Ti_2Fe_2As_4O$	*I4/mmm*	[Ti_2O] sheets and [Fe_2As_2]	superconducting	119
LaMnAsO	*P4/nmm*	[Mn-As] and [La-O] layers	Ca doping, antiferromagnetic ordering	120
NdMnAsO	*P4/nmm*	[Mn-As] and [Nd-O] layers	Sr doping magnetic properties	121
NdFeAsO	*P4/nmm*	[Fe-As] and [Nd-O] layers	Pressure phase transition, superconducting	122
$U_2Cu_2As_3O$	*P4/nmm*	[Cu-As], [U-O] slab	no properties	123
Ti_8BiO_7	*Cmmm*	[OTi_4] tetrahedra, [TiO_4Bi_2] octahedra	electrical resistivity	124
$(SrF)_2Ti_2Bi_2O$	*I4/mmm*	[Ti_2O] plane, [Ti_2Bi_2O]	superconductivity	13
Ce_2O_2Bi	*I4/mmm*	[Ce-O] layer	transport, magnetic properties	125–127
R_2O_2Bi (R=La, Ce, Pr, Nd, Sm, Eu, Gd, Ho, Er,	*I4/mmm*	Bi^{2-} square net [R_2O_2] layer	magnetic properties	128

Yb, Y)				
Eu_4Bi_2O	*I4/mmm*	[OEu_6] octahedra Bi coordinated by nine Eu atoms		[129]
Sm_4Bi_2O	*I4/mmm*	[$BiSm_9$], [OSm_6] octahedra		[130]
$Ba_2Cd_{2.13}Bi_3O$	*I4/mmm*	[Ba-O] layer [Cd-Bi] layer		[131]
Gd_3BiO_3	*C2/m*	[GdO_4] tetrahedra	thermoelectric properties	[132]
$Gd_8Bi_3O_8$	*C2/m*	[GdO_4] tetrahedra	thermoelectric properties	[132]
A_4X_2O (A=Ca, Sr, Ba; X=Sb, P, As, Bi)	*I4/mmm*	P surrounded by nine Ca atoms (tetragonal antiprism distorted) O atoms fill octahedral holes	electronic properties	[133]
Ba_3Sb_2O	*Pbam*	[Sb_2] and O anions separated by Ba cations		[134]
Ba_3Sb_4O	*P*-21/*c*	[Ba-Sb] units and [OBa_4] tetrahedra		[135]
KBa_4Bi_3O	*I4/mcm*	[Bi_2] units		[136,137]
CeZnPO	*P4/nmm*	[Ce-O] and [Zn-P] layers	phase transition	[138]
PrZnPO	*R*-3*m*	[Pr-O] and [Zn-P] layers	phase transition	[138]
$Ln_3Cu_4P_4O_2$ (Ln=La, Ce, Nd)	*I4/mmm*	[Cu_2P_2] layers [Ln_2O_2] sheets	electric and magnetic properties	[139]
$Sr_2VFeAsO_3$	*P4/nmm*	[FeAs] and [Sr_2VO_3] layers	superconductor	[140,141]
$Sr_3Sc_2Fe_2As_2O_5$	*I4/mmm*	[FeAs] layer and [$Sr_3Sc_2O_5$] blocks	electric and magnetic properties	[142]
$Na_2Ti_2As_2O$	*I4/mmm*	[ONa_2Ti_4] octahedra		[143]
$Sc_4Yb_4Sb_4O$	*I4/mmm*	[YbSb] double layer		[144]
$BaTi_2Pn_2O$ (Pn=As, Sb, Bi)	*P4/mmm*	[Ti_2Pn_2O] layers and Ba layers	electronic and magnetic properties	[145–147]
$Ba_5Cd_2Sb_4O_2$	*C2/m*	[$CdSb_4$] tetrahedra and [Ba-O] slabs		[148]
$Nd_{10}Au_3As_8O_{10}$	*I4/m*	[NdO] layers and [$Au_3(As_2)_4$] units	magnetic and electronic properties	[149]
$Sm_{10}Au_3As_8O_{10}$	*I4/m*	[SmO] layers and [$Au_3(As_2)_4$] units	magnetic and electronic properties	[149]
HT/LT-$Nd_{10}Pd_3As_8O_{10}$	*I4/m*	[NdO] layers and [$Pd_3(As_2)_4$] units	magnetic and electronic properties	[150]
$Sm_{10}Pd_3As_8O_{10}$	*C2/c*	[SmO] layers and [$Pd_3(As_2)_4$] units	magnetic and electronic properties	[150]
RE_2AuP_2O (RE=La, Ce, Pr)	*C2/m*	[La_2O] chains [AuP_2] units		[151,152]

Table S7. Selected other heteroanionic combinations with structural information and physical properties (N-Cl, S-Cl, Se-Cl, P-Cl, P-Br, etc.).

Compound	Space group	BBU	Property	Ref
TiNCl	*Pmmn*		Eg (cal) = 0.63 eV	[153]
LiTiNC	*Pmmn*		T_c = 16.5, fraction=0.5%	[153]

$Na_{0.22}TiNCl_{0.98}$	*Bmmb*		A_xTiNCl also became superconductors with much higher T_cs of ~ 16.3 K. Fraction = 13.3%	153
$K_{0.22}TiNCl_{0.90}$	*Immm*		A_xTiNCl also became superconductors with much higher T_cs of ~ 16.3 K. Fraction = 31.0%	153
$Rb_{0.19}TiNCl_{0.75}$	*Immm*		A_xTiNCl also became superconductors with much higher T_cs of ~ 16.3 K. Fraction = 4.3%	153
Li_xZrNCl	*R*-3*mH*		Black crystal. The structural transformation by Li intercalation is interpreted as the sliding of $[ZrNCl]_2$ slabs due to an electrostatic force. T_c = 12.5 K	154
β-ZrNCl	$R\overline{3}m$		pale yellow-green; Eg ~3 eV	155,156
ThNCl	*P*4/*nmm*		Eg (exp) = 3.79 eV	157
β-HfNCl	*R*-3*mH*		T_c=25.5K	158
$MoNCl_3$	*P*-1			159
Zn_2NCl	*Pna*21		mid-IR NLO, Eg =3.21 eV, LDT = 20.7×AGS, SHG = 0.9×AGS	10
$Ba_{15}Ta_{15}N_{33.66}Cl_4$	*P*-62*c*	TaN_4 tetrahedra		160
$Zn_7(P_{12}N_{24})Cl_2$	*I*-43*m*	PN_4 tetrahedra	$[P_{12}N_{24}]$-Gerust ist aus $[P_4N_4]$- und $[P_6N_6]$-Ringen	161
W_6PCl_{17}	*Imm*2		phosphorus-centered hexanuclear tungsten cluster, $(W_6PCl_{11})Cl_4^aCl_{4/2}^{a-a}$ chains form a hexagonal stick packing structure	162
$W_4(PCl)Cl_{10}$	*C*12/*m*1		Jahn–Teller distorted tetranuclear tungsten cluster that is interconnected into a layered $[W_4(\mu_4\text{-}PCl)Cl_6^iCl_{8/2}^{a-a}$ structure containing a chloro-phosphinidene ligand.	162
$Sr_3P_5N_{10}Cl$	*Pnma*		Excitation with UV to blue light (λ_{exc}=420 nm) induces natural-white	162

			($Ba_3P_5N_{10}Br:Eu^{2+}$), orange ($Ba_3P_5N_{10}Cl:Eu^{2+}$), and deep-red emission ($Sr_3P_5N_{10}X:Eu^{2+}$)	
$Sr_3P_5N_{10}Br$			Excitation with UV to blue light (λ_{exc}=420 nm) induces natural-white ($Ba_3P_5N_{10}Br:Eu^{2+}$), orange ($Ba_3P_5N_{10}Cl:Eu^{2+}$), and deep-red emission ($Sr_3P_5N_{10}X:Eu^{2+}$)	[162]
$Ba_3P_5N_{10}Cl$			Excitation with UV to blue light (λ_{exc}=420 nm) induces natural-white ($Ba_3P_5N_{10}Br:Eu^{2+}$), orange ($Ba_3P_5N_{10}Cl:Eu^{2+}$), and deep-red emission ($Sr_3P_5N_{10}X:Eu^{2+}$)	[162]
$Ba_3P_5N_{10}Br$			Excitation with UV to blue light (λ_{exc}=420 nm) induces natural-white ($Ba_3P_5N_{10}Br:Eu^{2+}$), orange ($Ba_3P_5N_{10}Cl:Eu^{2+}$), and deep-red emission ($Sr_3P_5N_{10}X:Eu^{2+}$)	[162]
Sr_2P_7Cl	*C*12/*c*1	heptaphosphanortricyclane P_7^{3-} clusters	all electron-balanced wide band gap semiconductors, Eg = 1.9eV	[163]
Sr_2P_7Br	*P*21/3		Eg = 2.1 eV	[163]
$P_6N_7Cl_9$	*C*12/*c*1	a non-planar condensed ring structure		[164]
$P_2B_4Cl_4$	*Pbna*			[165]
PCl_5TaCl_5	*P*-1	tetrahedral cations PCl_4^+, and octahedral anions $NbCl_6^-$ and $TaCl_6^-$		[166]
PCl_5NbCl_5	*P*-1			[166]
PCl_4TeCl_5	*I*2*mb*		tetrahedral $[PCI_4]^+$ cations and polymeric infinite chain anions $[TeCl_5]_n^{n-}$	[167]
PCl_4SnCl_5	*Cmma*			[168]
Li_6PS_5Cl	*F*-43*m*		S^{2-} anions in half of the tetrahedral voids and PS_4^{3-} tetrahedra on the	[169,170]

			octahedral sites the effect of lattice polarizability on the ionic conductivity	
Hg_2PCl_2	*I*12/*m*1	(P_2Hg_6) Octahedron	Hg6 octahedron centered with a P_2^{4-} dumbbell	[171]
$La_3Zn_4P_6Cl$	*Cmcm*	two-dimensional $^{\infty}{}_{2}[Zn_4P_6]^{8-}$ layers separated by one-dimensional $^{\infty}{}_{1}[Cl_2La_3]^{8+}$ chains	Semiconductors, Eg = 0.45 eV	[172]
$Hg_6SnP_4Cl_6$	*P*213	$[Hg_6P_4Cl_3]^+(SnCl_3)^-$	Supramolecular inorganic compound	[173]
$(NPBr_2)_3$	*Pcmn*			[174]
$Ge_{38}P_8Br_8$	*P*-43*n*			[175]
La_2Br_2P	*P*-3*m*1		Phosphide Halides; Structure X-M-Z-M-X in M_2X_2Z	[176]
$Sn_{24}P_{19.60}Br_8$	*Pm*-3 *n*		cationic clathrate. The Sn(1) is tetrahedrally coordinated by three phosphorus atoms and one tin atom, Sn(2). The halogen atoms are trapped in the cavities of the clathrate framework. Two types of the cavities: the pentagonal dodecahedral and the tetrakaidecahedral, which occur in a 2:6 ratio in the unit cell	[177]
$Zn_6S_5Cl_2$	*Cmcm*	1-D tunnel-like structure	Ten zinc atoms and ten sulfur atoms interconnect to each other to form a cubane-like structure. Eg (exp) = 2.71 eV	[6]
$Hg_3ZnS_2Cl_4$	*P*63*mc*		2-D layered structure which contains interconnected 12-membered Hg6S3Cl3 rings with chair-like conformation, and the layers sandwich the $ZnSCl_3$ tetrahedra. Eg (exp) = 2.65 eV	[6]
$WSCl_4$	*P*121/*c*1		The arrangement of the five ligands around the tungsten atom may be regarded as a regular square pyramid, with	[178,179]

			sulfur atom in the unique position.	
$Pb_3S_2Cl_2$	*I*-43*d*		Narrow size distribution and size tunability over the range 7 to ∼30 nm, Eg(cal) =2.02 eV	[180]
$Li_{15}P_4S_{16}Cl_3$	*I*-43*d*	PS4, LiS4, and Li(S_3Cl)	Solid-State Ionic Conductor	[181]
Ta_3SBr_7	*C*1*m*1			[182]
$Ge_4S_6Br_4$	*P*-1			[183]
Ag_3SBr	*Pm*-3*m*		The directions of Ag motion with large amplitude are nearly toward four face centers of a distorted S and Br tetrahedron. Phase transition beta-gamma. Superionic conductor	[184]
$K_2Ba_3Ge_3S_9Cl_2$	*P*63	distorted $[GeS4]^{4-}$ tetrahedra	Eg = 3.69 eV LIDT intensity (28.8 × AGS) SHG response (0.34 × AGS)	[185]
$Ag_6SnS_4Br_2$	*Pnma*			[186]
As_4S_3(CuCl)	*Pbcm*		Supramolecular	[187]
Ba_3GaS_4Cl	*Pnma*	BaX pseudolayers and isolated GaQ_4 tetrahedra	Eg =2.14 eV	[188]
$Ba_3KSb_4S_9Cl$	*Pnnm*		Eg =1.99 eV	[189]

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