Heavy pnictogen chalcohalides: synthesis, structure and properties of rediscovered semiconductors

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Electronic supplementary information

Table S1. Computed with various methods band gaps, electron and hole effective masses, ionization potentials, electron affinities and static dielectric constants for bulk 15 group oxyhalides and chalcohalides.

	Space Group (International S. G. number)	E_g [eV]	E_g direct [eV]	$m_{eff}(e)$ [me]	$m_{eff}(h)$ [me]	IP	EA	Ionic Dielectric constant ε_r	Method
Sb-O-F	*Pnma*	4.33	4.72	1.94	1.23	20.49			HSE+SOC[169]
Sb-O-Cl	*P2₁/C*		4.02	1	2.66	19.68			HSE+SOC [169]
Sb-S-Cl	*Pnam* (62)	2.18	2.51						EPM[199]
		2.31	2.73	0.51	0.64	5.80	3.37		HSE06-SOC[198]
		2.53		0.10	0.32				QSGW-SOC[198]
Sb-S-Br		2.21	1.72	0.26	0.57				EV-SOC[173]
		1.57							SR-GGA[211]
		2.16		0.52	3.6				NCPP-PBE-GW[200]
		2.29	2.32					105.15	HSE+SOC [169]
	*Pna*2$_1$ (33)	2.21							(GGA)E-V + SOC [228]
Sb-S-I	*Pnam* (62)	2.11							EPM[199]
		1.82	2.07	0.53	1.39			37.28	HSE+SOC [169]
		2.05							(GGA)E-V + SOC [228]
		1.445							LDA + PAW [177]
		1.28							PAW-PBE-SOC [171]
	*P*2$_1$2$_1$2$_1$ (19)	1.45	1.46	0.91	2.84			31.59	PAW-PBE-SOC [171]
	*Pna*2$_1$ (33)	1.45	1.60	1.31	2.06			69.72	PAW-PBE-SOC [171]
		2.11	1.60	1.25	2.06			69.38	HSE06-SOC[198]
		2.22	2.31			5.37	3.15		QSGW-SOC[198]
		2.05	2.42	0.43	0.57				EV-SOC[173]
		1.51		0.07	0.098				SR-GGA[211]
		1.45	1.66	0.21	0.27				NCPP-LDA[237]
	*Pna*2$_1$ (33)	1.49	1.56						NCPP-LDA[413]
		1.446	1.58						LDA+PAW[177]
Sb-Se-Br		0.23	0.47						NCPP-PBE[201]
Sb-Se-I		1.67	2.06						EPM[199]
		1.86	2.23	0.54	0.58	5.26	3.23		HSE06-SOC[198]
	Pnma (62)	2.03	1.29	0.59	4.37			43.94	QSGW-SOC[198]
		1.16		0.082	0.164				PAW-PBE-SOC [171]
		1.62	1.40	0.52	0.24				EV-SOC[173]
		1.29							SR-GGA[211]
		1.65		0.35	1.83				NCPP-PBE&GW[175]
		1.75	1.96					57.18	HSE+SOC [169]
		1.62							(GGA)E-V + SOC [228]
		1.26							LDA + PAW[177]
Sb-Te-I		0.89							PAW-PBE[179]
	C2/m	1.20	1.29	0.31	1.59			44.69	HSE+SOC [169]
		0.90							LDA + PAW [177]

		0.68							GGA-PBE + SOC [203]
		0.89							PBE [179]
		1.82							PBE [204]
		1.32							Empirical methods [205]
Bi-O-F		3.41	3.41						SR-PBE[184]
		3.0	3.0						PBE[183]
	P4/*nmmS* (129)	3.07	3.07	0.31	0.90				PBE-D3-SOC[206]
		4.18	4.18						mBJ-SOC[206]
		4.18		0.5	12.5	8.23	3.87		SR-PAW-HSE06-D3-SOC[225]
		4.43	3.94	0.52	2.35			102.1	HSE+SOC[169]
			3.07						PBE-GGA + vdW + SO [206]
Bi-O-Cl		2.69							SR-PBE[184]
		2.60							PBE[183]
	P4/*nmmS* (129)	2.63		0.46	0.27				PBE-D3-SOC[206]
		3.72							mBJ-SOC[206]
		3.37		0.3	0.8	7.94	4.35		SR-PAW-HSE06-D3-SOC[225]
	P4/nmm	3.29	3.80	m_e=0.39,m_h=1.33				51.74[169]	HSE+SOC[169]
		2.63							PBE-GGA + D3, HSE [180]
		3.66							PBE-GGA + vdW + SOC [206]
		2.38							PBE + PAW + SO [182]
Bi-O-Br		2.21							SR-PBE[184]
		2.24							PBE[183]
	P4/*nmmS* (129)	2.11		5.68	0.2				PBE-D3-SOC[206]
		2.93							mBJ-SOC[206]
		2.82		0.3	0.7	7.55	4.65		SR-PAW-HSE06-D3-SOC[225]
	P4/nmm	2.86	3.09	m_e=0.36, m_h=1.72				44.62	HSE+SOC [169]
		2.11							PBE-GGA + D3, HSE [180]
		3.08							PBE-GGA + vdW + SO [206]
Bi-O-I		1.38		0.37	3.75				PAW-PBE-SOC [171]
		1.62							SR-PBE[184]
		1.63							PBE[183]
	P4/*nmmS* (129)	1.46	1.49	6.34	0.54			46.32	PBE-D3-SOC[206]
		2.11							mBJ-SOC[206]
		2.00			1.9	7.03	5.03		SR-PAW-HSE06-D3-SOC[225]
Bi-S-Cl		0.74	1.1						SCPM[197]
		1.40	1.54						NCPP-PBE[201]
		1.6	1.9						FLAPW-GGA[190]
		1.5							FLAPW-GGA[189]
Bi-S-Cl		0.74	1.1						SCPM[197]
		1.40	1.54						NCPP-PBE[201]
		1.6	1.9						FLAPW-GGA[190]
		1.5							FLAPW-GGA[189]
	Pnma		1.98[169]	0.51	2.91			37.53	
Bi-S-Br	*Pnma* (62)	1.39	1.55						SCPM[197]
		1.32	1.35	0.24	6.21			30.10	PAW-PBE-SOC [171]
		1.21	1.39						NCPP-PBE[201]
	Pnma		1.89[169]	m_e=0.52,m_h=3.73				35.75	
Bi-S-I		1.5	1.65						SCPM[197]
	Pnam (62)	1.18	1.32	0.53	4.79			29.59	PAW-PBE-SOC [171]
	Pnma (62)	1.78	1.82	0.68	0.36	6.4	4.9	36.8	HSE06-SOC[68]
		1.88							PAW-PBE[179]

		1.39	1.55						NCPP-PBE[201]
		1.57							FLAPW-GGA[188]
	Pnma	1.66	1.87	m_e=0.45,m_h=1.72				37.81	HSE+SOC [169]
		1.88							PBE [179]
Bi-Se-Cl		0.27	0.45						SCPM[197]
	Pnma	1.45	1.47	m_e=0.46,m_h=2.65				20.38	HSE+SOC[169]
Bi-Se-Br		0.87 1.14	0.97 1.25						SCPM[197] NCPP-PBE[201]
	Pnma	1.45	1.48	m_e=0.44,m_h=2.25				34.59	HSE+SOC[169]
Bi-Se-I		0.8	1.15						SCPM[197]
	Pnma (62)	0.91	1.03	0.25	5.89			26.83	PAW-PBE-SOC [171]
	Pnma (62)	1.50	1.60	0.51	0.28	6.2	5.0	35.8	HSE06-SOC[68]
		0.57	0.52						NCPP-PBE[201]
		1.35							FLAPW-GGA[50]
	Pnma	1.32	1.48	m_e=0.42,m_h=2.39				35.05	HSE+SOC[169]
Bi-Te-Cl		1.38							PAW-PBE[179]
		0.868							FLAPW-LDA-GW-SOC[207]
	P3m1	1.20	1.33						HSE+SOC[169]
		1.20							PBE + UPPW[192]
		0.67							PBE + SOC[208]
	P63mc	1.38							PBE [179]
Bi-Te-Br		1.09							PAW-PBE[179]
		1.09							FLAPW-PBE[156]
		0.28							FLAPW-PBE-SOC[156]
		0.65							FLAPW-LDA-GW-SOC[207]
	P3m1	1.10							PBE + UPPW[192]
		0.53							PBE[179]
		0.59							PBE[208]
		1.09							PBE[194]
Bi-Te-I		1.24							PAW-PBE[179]
		0.43							PAW-PBE-SOC[193]
		0.21							PAW-PBE-D2-SOC[193]
		0.17							PAW-PBEsol-SOC[195]
		1.2							FLAPW-PBE[202]
		0.28							FLAPW-PBE-SOC[202]
		0.4							FLAPW-LDA-GW-SOC[207]
	P3m1	0.90							HSE+SOC[169]
		0.80							PBE + UPPW[192]
		0.90							GGA+SOC[203]
		0.41							PBE[208]
		0.48							PBE[194]
		0.31							LDA + mBJ + SOC [209]
		1.24							PBE[179]

Table S2. BiOX (X = Cl, Br, I) and their photocatalytic applications.

	Samples	Photocatalytic applications	Range irradiation	Synthetic procedures	Ref.
1D template Nanostructure	BiOCl nanofibers	Completely RhB degraded within 60 min	UV	electro-spinning	356
	BiOCl fibers	75% MO mineralization in 110 min	UV	solvothermal synthesis (ethanol)	370
	BiOCl nanowire arrays	Almost 100% RhB degradation within 130 min	UV	sol-gel	367
2D intrinsic nanostructures	BiOCl plates	Completely MO degradation within 10 min	UV	hydrolysis	260
	BiOCl nanosheets	About 2 times higher RhB photodegradation rate than that on P25	UV	hydrolysis	340
		About 99% MO degradation within 45 min	UV	hydrothermal synthesis	366
	BiOCl nanoplates	Completely RhB disappearance within 8 min	Visible light	mannitol-assisted hydrothermal synthesis	373
	BiOCl lamellae	Good catalytic activity and selectivity in the oxidative coupling of the methane (OCM) reaction	ultrasonic irradiation	sonochemical method	414
	BiOBr lamellas	Completely RhB degraded within 30 min	Visible light	hydrolysis	337
		96% MO degraded within 120 min	Visible light	hydrothermal synthesis	358
	BiOI nanosheets	7 times higher photoactivity than that on irregular BiOI	Visible light	thermal annealing	368
	BiOX (X = Cl, Br, I) nanosheets	95.9% sodium pentachlorophenate (Na-PCP) degradation on BiOI within 1 h following BiOI > BiOBr > BiOCl	Xe-lamp	hydrolysis	332
3D assembled hierarchical architectures	BiOX (X = Cl, Br, I) nanoplate microspheres	80% MO degraded on BiOI within 3 h with the order BiOI > BiOBr > BiOCl	Visible light	solvothermal synthesis (ethylene glycol)	331
	BiOX (X = Cl, Br, I) hierarchical architectures	Completely MO degradation on BiOI within 60 min	UV-Vis	solvothermal synthesis (2-methoxyethanol, ethylene glycol)	372
	BiOCl porous nanospheres	Almost 100% RhB degraded within 2 h	Visible light	solvothermal synthesis (ethylene glycol)	341
	BiOCl nano-flowers	Completely MO degradation within 10 min	UV	solvothermal synthesis (pirydyne)	350
	BiOCl hierarchical architectures	Completely degrade RhB within 60 min	UV	solvothermal synthesis (ethylene glycol)	362
	BiOCl hierarchical self-assemblies	90.2% RhB degraded within 50 min	UV	hydrothermal synthesis	343
	BiOCl micro-flowers	99.3% RhB degraded within 15 min	Visible light	hydrothermal synthesis (glycerol + H_2O)	353
	BiOCl hierarchical flowers	90% MO degraded after 1 h	simulated sunlight	sonochemical route	360
	BiOCl 3D desert roses	Completely RhB degraded within 20 min	Visible light	Refluxing method	415
	BiOCl nano-flowers	Completely RhB degradation within 50 min	Visible light	hydrolysis	348
	BiOCl 3D flowers	100% RhB degraded within 80 min	Visible light	solution oxidation process	347
	BiOCl sub-microcrystals	99.5% RhB decomposed within 75 min	UV	hydrolysis	60
	BiOBr nanoplate microspheres	Nearly 30% NO removal within 10 min	Visible light	solvothermal synthesis (ethylene glycol)	346
	BiOBr	100% tetrabromobisphenol A decomposed within 15 min	simulated	solvothermal	355

	microspheres		sunlight	synthesis (ethylene glycol)	
		99% phenol decomposed within 80 min	UV	microwave-assisted solvothermal synthesis (DEG)	342
		90% *Micrococcus lylae* inactivated after 6 h	fluorescent light	solvothermal synthesis (TEG)	352
		95% RhB degraded within 40 min	Visible light	solvothermal synthesis (isopropanol + ethylene glycol)	364
		Higher MO drgradation than that on BiOBr bulk plates	Visible light	solvothermal synthesis (ethylene glycol)	361
	BiOBr 3D microspheres	Toluene conversion rate 2-fold larger than that on P25	simulated sunlight	solvothermal synthesis (ethanol)	369
	BiOBr mesoporous microspheres	Nearly 100% bisphenol A degradation within 90 min	simulated sunlight	solvothermal synthesis (ethanol)	359
	BiOBr porous nanospheres	RhB completely degraded within 105 min	Visible light	solvothermal synthesis (ethylene glycol)	363
	BiOBr hollow microspheres	100% RhB degraded in 15 min and 90% Cr(VI) reduced in 20 min	Visible light	solvothermal synthesis (2-methoxythanol)	354
	BiOBr micro-flowers	92.5% methylene blue (MB) degraded for 4.5 h	Visible light	solvothermal synthesis (ethylene glycol)	365
	BiOBr fullerene-like eggshells	Over 95% RhB degraded within 25 min	Visible light	ultrasound reaction and heating synthesis	416
	BiOI hierarchical structures	MO completely degraded within 50 min	Visible light	hydrothermal synthesis	345
	BiOI hollow microspheres	92% MO degraded within 3 h	Visible light	solvothermal synthesis (ethylene glycol)	351
	BiOI microspheres	94% tetracycline hydrochloride decomposed within 2 h	Visible light	direct precipitation	344
		97% phenol decomposed within 4 h	Visible light	chemical bath	349
	BiOI micro-flowers	80% RhB degraded within 4 h	Visible light	solvothermal synthesis (ethylene glycol)	383
		100% RhB degraded within 2 h	Visible light	direct precipitation	360

Table S3. Electrical properties of pnicnide chalcohalides

Compound	Specific resistivity, Ω·cm	Charge carrier mobility, $cm^2 V^{-1} sec^{-1}$	Ref
AsSI	>10^{13} (at room temperature) 10^{16} to 10^{12} (decreases with iodine concentration increase)		291 292
AsSBr	>$3 \cdot 10^{14}$ (for 60 at. % of sulphur and 3-9 at % of bromine) 10^{15} to 10^{12} (at 20 ˚C)		293 72
AsSeBr	10^{13} to 10^{11} (decreases with Br concentration increase)		72
AsTeI	10^{3} (low iodine content) to 10^{8} (high iodine content)	0.08 (at room temperature) 0.12 (at 90˚C) 10^{-2} to 10^{-1} ($As_{50}Te_{50-x}I_x$ (x = 0, 2, 20) glasses) 0.08 ($As_{53}Te_{43}I_4$ glass)	295 295 301 295, 304
AsTeBr		0.01 (at room temperature) 0.10 (at 90˚C)	295 295
SbSI	10^{10} to 10^{7} (glasses)	 50 to 100	72 308
SbSBr	10^{7} (crystal phase) 10^{10} (glass phase)		309
SbSeI	10^{8} (at room temperature)		143
SbSeBr	10^{7}		311
SbTeI		1.01	312
BiOCl	10^{10} to 10^{13} >10^{15} (<200K)		314 317
BiOI	>10^{15} (<200K)		317
BiOBr	>10^{15} (<200K)		317
BiSI	10^{8} to 10^{9} (Needle-like structures)		320
BiSBr	10^{3} to 10^{4}		308
BiSeI	~10^{10} to 10^{6} (decreases with temperature increase)		45
BiTeI		528 (at 77K) 242 (at 300K)	65
BiTeBr		1450 (at 77K) 310 (at 300K)	65

Additional references for Tables S1 and S2.

413. H. Akkus and A. Mamedov, *Open Physics*, 2007, **5**, 25.
414. J. Geng, W.-H. Hou, Y.-N. Lv, J.-J. Zhu and H.-Y. Chen, *Inorg. Chem.*, 2005, **44**, 8503-8509.
415. G. Cheng, J. Xiong and F. J. Stadler, *New J. Chem.*, 2013, **37**, 3207-3213.
416. C. Deng and H. Guan, *Mater. Lett.*, 2013, **107**, 119-122.