Supporting Information

Recent Advances in Rational Structure Design for Nonlinear Optical Crystals: Leveraging Advantageous Templates

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TableS1. Structures and optical properties of KBBF-type compounds.

	Compounds	Space group	SHG	Δ*n*	Absorption edge (nm)
KBBF	$KBe_2BO_3F_2$	*R*32	1.25KDP	0.088@400nm	147
Beryllium borates with KBBF-like structure	*γ*-$KBe_2B_3O_7$	$P2_1$	0.68KDP	/	186[a]
	β-$KBe_2B_3O_7$	$Pmn2_1$	0.75KDP	/	187[a]
	$RbBe_2B_3O_7$	$Pmn2_1$	0.79KDP	/	179[a]
	$Na_2CsBe_6B_5O_{15}$	*C*2	1.17KDP	/	192[a]
	$Na_2Be_4B_4O_{11}$	*P*1	1.3KDP	0.047@400nm	171
	$LiNa_5Be_{12}B_{12}O_{33}$	*Pc*	1.4KDP	0.045@1064nm	169
	$BaBe_2BO_3F_3$	$P6_3$	0.1KDP	0.081@200nm	<185
	$NH_4Be_2BO_3F_2$	*R*32	1.2KDP	0.057@400nm	153
	γ-Be_2BO_3F	*R*32	2.3KDP	0.0989@1064nm	144.8[a]
	Be_2BO_3F*	$P\bar{6}2c$	1.5KDP	0.086@400nm	138
Aluminum borates with KBBF-like structure	$BaAlBO_3F_2$	$P\bar{6}2c$	2.0KDP	0.0522@266nm	165
	$Rb_3Al_3B_3O_{10}F$	*P*31*c*	1.2KDP	/	<200
	$CsAlB_3O_6F$	$Pna2_1$	2.0KDP	0.091@1064nm[a]	166[a]
	$RbAlB_3O_6F$	$Pna2_1$	0.2KDP	0.0946@1064nm[a]	<200
	$Cs_{0.5}Rb_{0.5}AlB_3O_6F$	$P\bar{6}2c$	2.0KDP	/	<200
Zinc borates with KBBF-like structure	$BaZnBO_3F$	$P\bar{6}$	2.8KDP	/	223
	$CsZn_2B_3O_7$	*Cmc*21	1.5KDP	0.056@1064 nm	218
	$AZn_2BO_3X_2$ (A=NH_4, Na, K, Rb, X=Cl, Br)	*R*32	~2.53-3.01KDP	/	190-209
	$CsZn_2BO_3F_2$	*R*32	3.2KDP	/	190
	$CsZn_2BO_3Cl_2$	*R*32	2.8KDP	/	190
	$CsZn_2BO_3FCl$	*R*3	3.5KDP	/	190
Other borates with KBBF-like structure	$Li_4Sr(BO_3)_2$	*Cc*	2.0KDP	0.056@532nm	186
	Pb_2BO_3Cl	*P*321	9.0KDP	0.12@1064nm	<300
	Pb_2BO_3Br	*P*321	9.5KDP	0.055@1064nm[a]	~372
	Pb_2BO_3I	*P*321	10.0KDP	0.036@1064nm	<330
	$K_5Mg_2La_3(BO_3)_6$	*P*31*m*	3.1KDP	/	<200

[a] The data come from theoretical calculations. / = Not available. *Theoretically designed structure by using the first principles calculation method.

TableS2. Structures and optical properties of SBBO-type compounds.

	Compounds	Space group	SHG	Δ*n*	Absorption edge (nm)
SBBO	$SrBeB_2O_4$	$P\bar{6}2c$	3.8KDP	0.062@589nm[a]	155
Beryllium borates	$NaCaBe_2B_2O_6F$	*Cc*	0.4KDP	0.057@800nm	190[a]
Aluminum borates	$BaAl_2B_2O_7$	*R*32	1.7KDP	0.063@589.3nm	180
	$K_2Al_2B_2O_7$	*P*321	~0.9KDP	0.07@1064nm	180
	$K_3Ba_3Li_2Al_4B_6O_{20}F$	$P\bar{6}2c$	1.5KDP	0.063@532nm	190
	$K_3Sr_3Li_2Al_4B_6O_{20}F$	*R*32	1.7KDP	0.062@532nm	190
	$Rb_3Ba_3Li_2Al_4B_6O_{20}F$	$P\bar{6}2c$	1.5KDP	0.061@532nm	~198
	$Cs_2Al_2(B_3O_6)_2O$	$P6_3$	<1KDP	0.136@177.3	180
Other borates	$Ba_3Mg_3(BO_3)_3F_3$	$Pna2_1$	1.8KDP	0.045@532nm	184
	$Ba_3Mg_3(BO_3)_3F_3$	$P\bar{6}2m$	2.0KDP	/	<190
	$CaZn_2(BO_3)_2$	*Aba*2	3.8KDP	0.081@546nm	<190

[a] The data come from theoretical calculations. / = Not available.

TableS3. Structures and optical properties of ABF-type compounds.

	Compounds	Space group	SHG	Δ*n*	Absorption edge (nm)
ABF	$NH_4B_4O_6F$	$Pna2_1$	3.0KDP	0.117@1064nm	156
Alkali metal fluorooxoborates	CsB_4O_6F	$Pna2_1$	1.9KDP	0.114@1064nm	155
	NaB_4O_6F	*C*2	0.9KDP	0.120@1064nm	<180
	RbB_4O_6F	*C*2	0.8KDP	0.102@1064nm	<190
	$CsKB_8O_{12}F_2$	*P*321	1.9KDP	0.105@1064nm	<190
	$CsRbB_8O_{12}F_2$	$P\bar{6}2c$	1.1KDP	/	<190
	$CsKB_8O_{12}F_2{\cdot}CsI$	*R*32	0.6KDP	0.08@1064 nm	216
	$CsNH_4B_8O_{12}F_2{\cdot}CsI$	*R*32	/	/	/
Alkaline earth metal fluorooxoborates	$MgB_5O_7F_3$	$Cmc2_1$	2.4KDP	0.07@1064nm	<200
	$CaB_5O_7F_3$	$Cmc2_1$	2.0KDP	0.07@1064nm	<180
	$SrB_5O_7F_3$	$Cmc2_1$	1.6KDP	0.072@589nm	<180
	$BaB_2O_3F_2$	$P2_1$	/	/	<180
Other fluorooxoborates	$PbB_5O_7F_3$	$Cmc2_1$	6KDP	0.12@1064nm	225
	$PbB_2O_3F_2$	$P3_1m$	13KDP	/	220
	$SnB_2O_3F_2$	$P3_1m$	4KDP	/	250

[a] The data come from theoretical calculations. / = Not available.

TableS4. Structures and optical properties of LBO-type compounds.

	Compounds	Space group	SHG	Δ*n*	Absorption edge (nm)
LBO	LiB_3O_5	*Pna*2_1	d_{31}=-0.67 d_{32}=0.85 d_{33}=0.04	0.041@1064nm	155
Fluorine-directed modification	$Li_2B_6O_9F_2$	*Cc*	0.9KDP	0.07@1064nm	< 190
	LiB_6O_9F	*Pna*2_1	d_{15}=0.055 d_{24}=0.161 d_{33}=-0.011	0.06@1064nm	Bandgap=6.57[a]
	$Li_2B_3O_4F_3$	*P*$2_12_12_1$	d_{14}=0.088	0.05@1064nm	Bandgap=6.73[a]
	$LiNaB_6O_9F_2$	*Pnn*2	1.1KDP	0.067@1064nm	<190
	$RbB_3O_4F_2$	*P*2_1/*c*(CS)	/	0.09@1064nm	<190
Combining anion groups based on [B_3O_7]	$Cs_3[(BOP)_2(B_3O_7)_3]$	*R*3	3.0KDP	0.075@532nm	165
	$Rb_3B_{11}P_2O_{23}$	*P*1	2.5KDP	0.071@1064nm	168
“Structure-analogue”	$BC_2N_5H_6(OH)_2{\cdot}H_2O$	*P*$2_12_12_1$	0.5KDP	0.181@546.1nm	240
	$B(C_2N_5H_{6.5})_2(NO_3)_2$	*C*222	5.9KDP	0.148@546.1nm	243

[a] The data come from theoretical calculations. / = Not available.

TableS5. Structures and optical properties of *β*-BBO-type compounds.

	Compounds	Space group	SHG	Δ*n*	Absorption edge (nm)
β-BBO	*β*-BaB_2O_4	*R*3*c*	5.8KDP	0.114@1079nm	189
Cyanurates	$Ca_3(C_3N_3O_3)_2$	*R*3*c*	d_{22}=3.46	0.372@589.3nm	/
	$Ca_{3-x}Sr_x(C_3N_3O_3)_2$	*R*3*c*	>BBO	/	/
	α-$Sr_3(C_3N_3O_3)_2$	*Cc*	>BBO	/	/
	β-$Sr_3(C_3N_3O_3)_2$	*R*3*c*	d_{22}=3.93	0.374@589.3nm	420
	$K_6Cd_3(C_3N_3O_3)_4$	$I\bar{4}3d$	d_{14}=1.17	/	237
	$Eu_3(C_3N_3O_3)_2$	*R*3*c*	<BBO@800nm	/	/
	$KLi(HC_3N_3O_3)\cdot 2H_2O$	*Pna*2_1	5.3KDP	0.186@514nm	237
	$RbLi(HC_3N_3O_3)\cdot 2H_2O$	*Pna*2_1	2.1KDP	0.18@514.6nm[a]	239
	$RbNa(HC_3N_3O_3)\cdot 2H_2O$	*Pna*2_1	5.3KDP	0.194@532nm	247
	$Rb_{0.86}Cs_{0.14}Na(HC_3N_3O_3)\cdot 2H_2O$	*Pna*2_1	3KDP	0.238@532nm[a]	240
	$Sr(HC_3N_3O_3)\cdot 2H_2O$	*Ima*2	/	/	/
	$Sr(HC_3N_3O_3)\cdot 2.5H_2O$	*Pnc*2	d_{15}=5.00	0.341@800nm[a]	/
	$Cs_3Na(H_2C_3N_3O_3)_4\cdot 3H_2O$	*Pmn*2_1	0.67KDP	0.29@514nm[a]	227
	$Rb_3Na(H_2C_3N_3O_3)_4\cdot 3H_2O$	*Pmn*2_1	0.4KDP	0.389@532nm[a]	234
	$LiCl\cdot(H_3C_3N_3O_3)$	*R*3*m*	d_{22}=4.15	0.28@800nm[a]	215
Barbiturates	$Li_2(H_2C_4N_2O_3)\cdot 2H_2O$	*Fdd*2	10.8KDP	0.218@546nm	261
	$Ca(H_3C_4N_2O_3)_2\cdot H_2O$	*Aba*2	1.15KDP	0.490@546.1nm	269
Melamine	$2(C_3H_7N_6)^+2Cl^-\cdot H_2O$	*Cmc*2_1	4.3KDP	0.277@546 nm[a]	245
$[C_5H_6ON]^+$ cation	$[C_5H_6ON]^+[H_2PO_4]^-$	*P*$2_12_12_1$	3.0KDP	0.25@1064nm[a]	264
$[C_4H_6N_3]^+$ cation	$[C_4H_6N_3]^+[H_2PO_3]^-$	*P*2_1	2.0KDP	0.225@589.3nm	346
Other organic planar π-conjugated groups	$[C(NH_2)_3]_2[B_3O_3F_4(OH)]$	*P*1	1.4KDP	0.161@1064nm	195
	$C(NH_2)_3SO_3F$	*R*3*m*	5KDP	0.133@1064nm	200
	$C(NH_2)_3BF_4$	*R*3*m*	4.03KDP	0.120@546nm	193
	$[C(NH_2)_3]_6(PO_4)_2\cdot 3H_2O$	*Cc*	3.8KDP	0.078@1064nm	205
	$[C(NH_2)_3]_3PO_4\cdot 2H_2O$	*Pna*2_1	1.5KDP	0.055@546.1nm	250
	$(NH_4)_2C_2O_4\cdot H_2O$	*P*$2_12_12_1$	0.9KDP	0.1587@546nm	/
	$(NH_4)Sb_2C_2O_4F_5$	*P*$2_12_12_1$	1.1KDP	0.111@546nm	285
	$NaHC_4O_4\cdot H_2O$	*Pc*	2.3KDP	0.52@1064nm	350

[a] The data come from theoretical calculations. / = Not available.

TableS6. Structures and optical properties of KTP-type compounds.

	Compounds	Space group	SHG	Δ*n*	Bandgap (eV)
KTP	$KTiOPO_4$	$Pna2_1$	~8KDP	/	3.65
Phosphates	NH_4TiOPO_4	$Pna2_1$	quartz: 2400	/	/
	$TlTiOPO_4$	$Pna2_1$	quartz: 6000	/	/
	$AgTiOPO_4$	$Pna2_1$	/	/	/
	$KAlFPO_4$	$Pna2_1$	/	/	/
	$KGaFPO_4$	$Pna2_1$	/	/	/
	$KGeOPO_4$	$Pna2_1$	quartz: 3.3	/	/
	$KVOPO_4$	$Pna2_1$	/	/	/
	$KSnOPO_4$	$Pna2_1$	quartz: 0.5	/	/
	$KMg(H_2O)PO_4$	$Pmn2_1$	~1.14KDP	0.017@1064nm	>6.2
Sulfates	$NH_4SbSO_4Cl_2$	$P2_12_12_1$	~1.7KDP	/	4.54
	$RbSbSO_4Cl_2$	$P2_12_12_1$	2.7KDP	/	3.48
	$CsSbSO_4F_2$	$Pna2_1$	3.0KDP	0.112@1064nm	4.76
	$RbSbSO_4F_2$	$Pna2_1$	0.96KDP	/	4.75
	$NH_4SbSO_4F_2$	$Pna2_1$	0.7KDP	0.138@1064nm	4.67
	$NH_4BiSO_4Cl_2$	$P2_12_12_1$	4.8KDP	0.055@1064nm	<4.0
	$RbBiSO_4Cl_2$	$P2_12_12_1$	5.5KDP	0.056@1064nm	<4.0
	$KBiSO_4Cl_2$	$P2_12_12_1$	5.3KDP	0.047@1064nm	<4.0
	$K_2Mn_3(SO_4)_3F_2{\cdot}4H_2O$	$Cmc2_1$	0.2KDP	/	5.54
	$Rb_2Mn_3(SO_4)_3F_2{\cdot}2H_2O$	$Cmc2_1$	0.25KDP	/	5.55
	$KMgSO_4F$	$Pna2_1$	<1KDP	/	>6.52
	$KZnSO_4F$	$Pna2_1$	<1KDP	/	>6.52
Other KTP-type crystals	$Pb_2GaF_2(SeO_3)_2Cl$	$P2_1$	4.5KDP	/	4.32
	$ZrOF_4H_2$	$I\bar{4}2d$	2.2KDP	0.035@546nm	>6.52
	$HfOF_4H_2$	$I\bar{4}2d$	1.8KDP	0.026@546nm	>6.52

/ = Not available.

TableS7. Structures and optical properties of Perovskite framework-type and Aurivillius-type compounds.

	Compounds	Space group	SHG	Δ*n*	Absorption edge (nm)
Perovskite framework-type	$K_3B_6O_{10}Br$	*R*3*m*	3.0KDP	0.048@589.3 nm	182
	$K_3B_6O_{10}Cl$	*R*3*m*	4.0KDP	/	180
	$K_{3-x}Na_xB_6O_{10}Br$ (*x* = 0.13, 0.67)	*R*3*m*	~2.8KDP	/	<190
	$K_{3-x}Na_xB_6O_{10}Br$ (*x* =1.30, 2.20)	*Pnma*(CS)	/	/	<190
	$Na_3B_6O_{10}Br$	*Pnma*(CS)	/	/	290
	$Na_3B_6O_{10}Cl$	$P2_12_12_1$	d_{14} = −0.06[a]	/	<190
	$RbNa_2B_6O_{10}Cl$	$P2_12_12_1$	d_{14} = 0.03[a]	/	<190
	$RbNa_2B_6O_{10}Br$	*Pnma*(CS)	/	/	<190
	$Rb_3B_6O_{10}Cl$*	$P2_12_12_1$	2.2KDP	0.047@532 nm	6.56
Aurivillius-type	$BaClBF_4$	$Pmn2_1$	0.2KDP	/	180
	α-$BaBOF_3$	$P2_1$	d_{16} = 0.21, d_{14} = 0.05, d_{22} =-0.33, d_{23} = 0.24[a]	/	<200
	$BaBOF_3$*	*Cc*	d_{11} = -0.19, d_{12} = -0.10, d_{13} = 0.003, d_{15} = 0.03, d_{24} = 0.07, d_{22} = -0.18, d_{24} = -0.04[a]	/	<200
	β- $BaBOF_3$	$P2_1/c$(CS)	/	/	<200
	γ-$BaBOF_3$	$P2_1/c$(CS)	/	/	<200

[a] The data come from theoretical calculations. / = Not available. *Theoretically designed structure by using the first principles calculation method.

TableS8. Structures and optical properties of Diamond Like-type compounds.

	Compounds	Space group	SHG	Δ*n*(1064nm)	Bandgap (eV)
AGS	$AgGaS_2$	$I\bar{4}2d$	d_{36} =13.40	0.039	2.73
Binary and ternary diamond like structures	*α*-ZnS	$F\bar{4}3m$	d_{36} = 15.29	0	3.60
	β-ZnS	$P6_3mc$	d_{33} = -12.35	0.004	3.49
	GeS_2	$I\bar{4}2d$	d_{36} = 12.52[a]	0.050[a]	3.85[a]
	Ga_2S_3	*Cc*	d_{13} = 15.46[a]	0.041[a]	2.80
	$AgAlS_2$	$I\bar{4}2d$	d_{36} = 4.88[a]	0.047[a]	3.20
	$AgGaS_2$	$I\bar{4}2d$	d_{36} = 13.40	0.053	2.73
	$LiAlS_2$	$Pna2_1$	d_{33} = 13.37[a]	0.014[a]	4.68
	$LiGaS_2$	$Pna2_1$	d_{33} = 10.70	0.040	4.15[a]
	Cu_3SbS_4	$I\bar{4}2d$	d_{36} = -66.06[a]	0.072[a]	0.88
	Cu_3AsS_4	$Pmn2_1$	d_{33} = -80.01[a]	0.230[a]	1.34
	Li_3PS_4	$Pmn2_1$	d_{33} = 4.32[a]	0.016[a]	3.68[a]
	Cu_3PS_4	$Pmn2_1$	d_{33} = -6.79[a]	0.048[a]	2.51
	Ag_3PS_4	$Pmn2_1$	d_{33} = -7.58[a]	0.039[a]	2.88[a]
	$HgGa_2S_4$	$I\bar{4}$	d_{36} = 31.5	0.054	2.84
	$CdGa_2S_4$	$I\bar{4}$	d_{36} = 15.83[a]	0.042[a]	3.44
	$ZnGa_2S_4$	$I\bar{4}$	d_{36} = 11.92[a]	0.029[a]	3.60
	$Zn_3(PS_4)_2$	$P\bar{4}n2$	d_{pow} = 15.92	0.035[a]	3.07
	$InPS_4$	$I\bar{4}$	d_{36} = 25	0.048	3.12
Quaternary diamond like structures	$LiZnPS_4$	$I\bar{4}$	d_{pow} = 11.70	0.072[a]	3.44
	$AgZnPS_4$	$Pna2_1$	d_{pow} = 23.40	0.051[a]	2.76
	$AgCd_2GaS_4$	$Pmn2_1$	d_{33} = -26.98[a]	0.059[a]	2.15
	$CuZn_2AlS_4$	$I\bar{4}_2m$	d_{36} = 7.94[a]	0.006[a]	1.69
	$Ag_4CdGe_2S_7$	*Cc*	d_{36} =14.51	/	2.45
	$Ag_4HgGe_2S_7$	*Cc*	d_{36} =23.07	/	2.17
	$Li_4HgGe_2S_7$	*Cc*	1.5AGS	/	3.11
	Cu_2CdSnS_4	$I\bar{4}_2m$	d_{36} = -25.42[a]	0.134[a]	0.92
	Cu_2HgGeS_4	$I\bar{4}_2m$	d_{36} = 44.23[a]	0.024[a]	1.12[a]
	Cu_2ZnSnS_4	$I\bar{4}$	d_{36} = 32.62[a]	0.141[a]	1.50
	Li_2CdGeS_4	$Pmn2_1$	d_{33}=11.92[a]	0.023[a]	3.10
	Li_2CdSnS_4	$Pmn2_1$	d_{33}=8.74[a]	0.018[a]	3.26
	α-Cu_2ZnSiS_4	$Pmn2_1$	d_{33}=-10.06[a]	0.052[a]	3.00
	Li_2HgSiS_4	$Pmn2_1$	0.8AGS	/	2.68
	Li_2HgGeS_4	$Pmn2_1$	3.0AGS	/	2.46
	Li_2HgSnS_4	$Pmn2_1$	4.0AGS	/	2.32
	Li_2CdSiS_4	$Pmn2_1$	1.0AGS	/	3.76
	Li_2MnGeS_4	$Pna2_1$	d_{33}=9.92[a]	0.010[a]	3.07
	α-Li_2MnSnS_4	$Pna2_1$	d_{33}=6.25[a]	0.011[a]	3.00
	Li_2ZnSiS_4	$Pna2_1$	1.1AGS	/	3.90
	α-Li_2ZnGeS_4	$Pna2_1$	2.0AGS	/	4.07

	Li_2ZnSnS_4	*Pn*	d_{11}=12.84[a]	0.015[a]	2.87
	Ag_2ZnSiS_4	*Pn*	d_{11}=11.60[a]	0.034[a]	3.28
	β-Cu_2ZnSiS_4	*Pn*	d_{11}=12.02[a]	0.035[a]	3.20
	β-Li_2MnSnS_4	*Pn*	/	/	2.60[a]
	β-Li_2ZnGeS_4	*Pn*	0.7AGS	/	3.49
Diamond like-type metal selenides	$Li_2ZnGeSe_4$	*Pn*	$\chi^{(2)}$=19	/	1.86
	$Li_2ZnSnSe_4$	*Pn*	$\chi^{(2)}$=23	/	1.87
	$Li_2MnSnSe_4$	$Pmn2_1$	0.5AGS	/	2.03
	$Li_2CdGeSe_4$	$Pna2_1$	$\chi^{(2)}$=25.6	/	2.50
	$Li_2CdSnSe_4$	$Pna2_1$	$\chi^{(2)}$=25.3	/	2.20
	$RbGaSn_2Se_6$	*R*3	4.2AGS	0.051@2050 nm	1.80
	$RbInSn_2Se_6$	*R*3	4.8AGS	0.067@2050 nm	1.92
	$Li_4HgSn_2Se_7$	*Cc*	3.6AGS	/	2.10

[a] The data come from theoretical calculations. / = Not available.