Electronic Supplementary Information:

Large Optical Polarizability Causing Positive Effects on Birefringence of Planar-Triangular BO_3 Groups in Ternary Borates

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Table S6 Calculated optical permittivity and polarisabilities (*f*–>infinity) of ternary borates α-/β-$TM_3(BO_3)_2$ (TM = Zn, Cd), $Cd_2B_2O_5$, and $M_3(BO_3)_2$ (M = Hg, Mg, Ca, Sr).

Table S7 The BO_3 groups density (N/V) of ternary borates α-/β-$TM_3(BO_3)_2$ (TM = Zn, Cd), $Cd_2B_2O_5$, and $M_3(BO_3)_2$ (M = Hg, Mg, Ca, Sr).

Figure S1 Crystal structures of ternary borates α-$Zn_3(BO_3)_2$ (a), β-$Zn_3(BO_3)_2$ (b), α-ZnB_4O_7 (c), β-ZnB_4O_7 (d), α-$Cd_3(BO_3)_2$ (e), β-$Cd_3(BO_3)_2$ (f), $Cd_2B_2O_5$ (g), CdB_4O_7 (h), $Hg_3(BO_3)_2$ (i), α-HgB_4O_7 (j), β-HgB_4O_7 (k) , and $M_3(BO_3)_2$ (M = Mg, Ca, Sr) (l-n).

Figure S2 Calculated band structures for ternary borates α-$Zn_3(BO_3)_2$ (a), β-$Zn_3(BO_3)_2$ (b), α-ZnB_4O_7 (c), β-ZnB_4O_7 (d), α-$Cd_3(BO_3)_2$ (e), β-$Cd_3(BO_3)_2$ (f), $Cd_2B_2O_5$ (g), CdB_4O_7 (h), $Hg_3(BO_3)_2$ (i), α-HgB_4O_7 (j), β-HgB_4O_7 (k), and $M_3(BO_3)_2$ (M = Mg, Ca, Sr) (l-n) by GGA functional, all of borates calculated band gaps by the GGA and HSE06 functional (o).

Figure S3 Density/partial density of states of ternary borates α-$Zn_3(BO_3)_2$ (a), β-$Zn_3(BO_3)_2$ (b), α-ZnB_4O_7 (c), β-ZnB_4O_7 (d), α-$Cd_3(BO_3)_2$ (e), β-$Cd_3(BO_3)_2$ (f), $Cd_2B_2O_5$ (g), CdB_4O_7 (h), $Hg_3(BO_3)_2$ (i), α-HgB_4O_7 (j), β-HgB_4O_7 (k) , and $M_3(BO_3)_2$ (M = Mg, Ca, Sr) (l-n).

Figure S4 Ternary borates α-/β-$TM_3(BO_3)_2$ (TM = Zn, Cd), $Cd_2B_2O_5$, and $M_3(BO_3)_2$ (M = Hg, Mg, Ca, Sr): compared with the HSE06 band gaps (a) and O (2*p*) bandwidth (b).

Figure S5 Calculated birefringence Δ*n* of ternary borates α-$Zn_3(BO_3)_2$ (a), β-$Zn_3(BO_3)_2$ (b), α-ZnB_4O_7 (c), β-ZnB_4O_7 (d), α-$Cd_3(BO_3)_2$ (e), β-$Cd_3(BO_3)_2$ (f), $Cd_2B_2O_5$ (g), CdB_4O_7 (h), $Hg_3(BO_3)_2$ (i), α-HgB_4O_7

(j), β-HgB_4O_7 (k), and $M_3(BO_3)_2$ (M = Mg, Ca, Sr) (l-n).

Figure S6 Borates α-$Cd_3(BO_3)_2$ and $Cd_2B_2O_5$: IR spectra and thermal analysis. (a) and (b) are IR and thermal of α-$Cd_3(BO_3)_2$, (c) and (d) are those of $Cd_2B_2O_5$.

Figure S7 Calculated IR spectra of α-$Cd_3(BO_3)_2$ (a) and $Cd_2B_2O_5$ (b).

Table S1 Summary of crystallographic data of 14 ternary borates containing d^{10} configuration cations.

Compounds	Space group	Crystallographic data		ICSD number
		a, ***b***, ***c*** **(Å)**	**α, β, γ (°)**	
$Cd_2B_2O_5$[1]	*P*-1	*a* = 3.4414(3), *b* = 6.3570(6), *c* = 9.9389(9)	α = 105.474(6), β = 90.842(6), γ = 91.969(6)	238992-ICSD
α-$Zn_4O(BO_3)_2$[2]	*I*-43*m*	*a* = *b* = *c* = 7.480(3)	α = β = γ = 90	261810-ICSD
β-$Zn_4O(BO_3)_2$[3]	*R*-3*c*	*a* = *b* = *c* = 9.9115(4)	α = β = γ = 48.602(1)	72943-ICSD
α-ZnB_4O_7[4]	*Pbca*	*a* = 8.1093(2), *b* = 8.6340(2), *c* = 13.7200(3)	α = β = γ = 90	424545-ICSD
β-ZnB_4O_7[5]	*Cmcm*	*a* = 10.850(1), *b* = 6.489(1), *c* = 5.173(1)	α = β = γ = 90	412688-ICSD
α-$Zn_3(BO_3)_2$[6]	*P*-1	*a* = 6.302(2), *b* = 8.248(1), *c* = 10.020(1)	α = 89.85(1), β = 89.79(1), γ = 73.25(1)	155112-ICSD
β-$Zn_3(BO_3)_2$[7]	*C*2/*c*	*a* = 23.83041(8), *b* = 5.04360(3), *c* = 8.38073(5)	α = γ = 90, β = 102.95	193238-ICSD
CdB_2O_4[8]	*P*63	*a* = *b* = 8.8521(16), *c* = 7.1672(8)	α = β = 90, γ = 120	419180-ICSD
CdB_4O_7[9]	*Pbca*	*a* = 8.21(1), *b* = 8.70(1), *c* = 14.18(2)	α = β = γ = 90	14361-ICSD
α-$Cd_3(BO_3)_2$[10]	*Pnnm*	*a* = 5.9680(10), *b* = 4.7860(10), *c* = 9.012(2)	α = β = γ = 90	240724-ICSD
β-$Cd_3(BO_3)_2$[11]	*P*-1	*a* = 6.1114(5), *b* = 6.1463(5), *c* = 7.4232(6)	α = 76.521(3), β = 80.730(3),γ = 82.461(3)	427222-ICSD
$Hg_3(BO_3)_2$[12]	*R*-3*c*	*a* = *b* = 8.8936(9), *c* = 13.052(3)	α = β = 90, γ = 120	409688-ICSD
α-HgB_4O_7[13]	*Pbca*	*a* = 8.3994(13), *b* = 8.8066(6), *c* = 14.1370(17)	α = β = γ = 90	281287-ICS
β-HgB_4O_7[14]	$Pmn2_1$	*a* = 10.656(2), *b* = 4.3810(9), *c* = 4.1872(8)	α = β = γ = 90	415347-ICSD

Table S2 Space groups, calculated band gaps and birefringence values Δ*n* of ternary borates α-/β-$TM_3(BO_3)_2$ (TM = Zn, Cd), $Hg_3(BO_3)_2$, α-/β-TMB_4O_7 (TM = Zn, Hg), CdB_4O_7, $Cd_2B_2O_5$, and $M_3(BO_3)_2$ (M = Mg, Ca, Sr).

Classification	Compounds	Space group	Band gap (eV)		Δ*n* (@ 1064 nm)
			GGA	HSE06	
Zn cations	**α-$Zn_3(BO_3)_2$**	*P*-1	2.98	4.62	0.077
	β-$Zn_3(BO_3)_2$	*C*2/*c*	2.75	4.80[15]	0.078
	α-ZnB_4O_7	*Pbca*	4.72	6.55	0.036
	β-ZnB_4O_7	*Cmcm*	5.33	7.38	0.025
Cd cations	**α-$Cd_3(BO_3)_2$**	*Pnnm*	2.21	3.04	0.035
	β-$Cd_3(BO_3)_2$	*P*-1	2.31	3.16	0.072
	$Cd_2B_2O_5$	*P*-1	3.23	4.18	0.087
	CdB_4O_7	*Pbca*	4.71	5.67	0.041
Hg cations	**$Hg_3(BO_3)_2$**	*R*-3*c*	3.33	3.87	0.239
	α-HgB_4O_7	*Pbca*	3.22	4.41	0.037
	β-HgB_4O_7	$Pmn2_1$	2.30	3.43	0.021
Alkaline-earth cations	**$Mg_3(BO_3)_2$**	*Pnmn*	5.47	7.15	0.029
	$Ca_3(BO_3)_2$	*R*-3*c*	5.24	6.60	0.105
	$Sr_3(BO_3)_2$	*R*-3*c*	4.81	6.23	0.099

Table S3 Mulliken charge population of different atoms in ternary borates α-/β-$TM_3(BO_3)_2$ (TM = Zn, Cd), $Hg_3(BO_3)_2$, α-/β-TMB_4O_7 (TM = Zn, Hg), CdB_4O_7, $Cd_2B_2O_5$, and $M_3(BO_3)_2$ (M = Mg, Ca, Sr).

Species	*s*	*p*	*d*	Total	Charge (*e*)	Bond	Population
α-$Zn_3(BO_3)_2$							
Zn	0.33	0.59	9.98	10.90	1.10	B-O	0.85
B	0.55	1.70	0.00	2.25	0.75	Zn-O	0.35
O	1.79	5.02	0.00	6.81	−0.81	/	/
β-$Zn_3(BO_3)_2$							
Zn	0.31	0.59	9.98	10.88	1.12	B-O	0.85
B	0.55	1.71	0.00	2.26	0.75	Zn-O	0.33
O	1.78	5.02	0.00	6.81	−0.81	/	/
α-ZnB_4O_7							
Zn	0.15	0.37	9.99	10.51	1.49	B-O	0.71
B	0.52	1.56	0.00	2.07	0.93	Zn-O	0.23
O	1.74	5.01	0.00	6.74	−0.74	/	/
β-ZnB_4O_7							
Zn	0.02	0.44	9.99	10.46	1.54	B-O	0.66
B	0.59	1.56	0.00	2.15	0.85	Zn-O	0.23
O	1.73	4.98	0.00	6.71	−0.71	/	/
α-$Cd_3(BO_3)_2$							
Cd	0.27	0.54	9.99	10.80	1.20	B-O	0.84
B	0.60	1.72	0.00	2.32	0.68	Cd-O	0.15
O	1.81	5.01	0.00	6.83	−0.83	/	/
β-$Cd_3(BO_3)_2$							
Cd	0.30	0.50	9.99	10.79	1.21	B-O	0.84
B	0.58	1.74	0.00	2.31	0.70	Cd-O	0.16
O	1.81	5.03	0.00	6.84	−0.84	/	/
$Cd_2B_2O_5$							
Cd	0.25	0.47	9.99	10.71	1.30	B-O	0.83
B	0.54	1.69	0.00	2.23	0.77	Cd-O	0.32

O	1.78	5.05	0.00	6.82	−0.82	/	/
				CdB_4O_7			
Cd	0.10	0.28	9.99	10.37	1.63	B-O	0.77
B	0.52	1.56	0.00	2.08	0.92	Cd-O	0.16
O	1.74	5.02	0.00	6.76	−0.76	/	/
				$Hg_3(BO_3)_2$			
Hg	0.77	0.37	9.79	10.94	1.06	B-O	0.85
B	0.54	1.70	0.00	2.23	0.77	Hg-O	0.24
O	1.80	4.98	0.00	6.79	−0.79	/	/
Species	***s***	***p***	***d***	**Total**	**Charge (*e*)**	**Bond**	**Population**
				α-HgB_4O_7			
Hg	0.33	0.29	9.96	10.59	1.41	B-O	0.71
B	0.52	1.55	0.00	2.06	0.94	Hg-O	0.15
O	1.74	5.00	0.00	6.74	−0.74	/	/
				β-HgB_4O_7			
Hg	0.26	0.32	9.99	10.57	1.43	B-O	0.65
B	0.58	1.57	0.00	2.15	0.86	Hg-O	0.02
O	1.73	4.96	0.00	6.69	−0.69	/	/
				$Mg_3(BO_3)_2$			
Mg	0.28	0.39	0.00	0.67	1.33	B-O	0.85
B	0.58	1.77	0.00	2.35	0.65	Mg-O	0.19
O	1.79	5.09	0.00	6.88	−0.88	/	/
				$Ca_3(BO_3)_2$			
Ca	2.14	6.00	0.56	8.70	1.30	B-O	0.80
B	0.51	1.71	0.00	2.22	0.78	Ca-O	0.09
O	1.80	5.11	0.00	6.91	−0.91	/	/
				$Sr_3(BO_3)_2$			
Sr	2.13	5.99	0.64	8.76	1.24	B-O	0.80
B	0.53	1.71	0.00	2.24	0.76	Sr-O	0.09
O	1.80	5.07	0.00	6.87	−0.87	/	/

Table S4 Calculated dipole moment (***P***), anisotropy polarizability (**Δ*α***), largest hyperpolarizability tensor (|***β***$_{max}$|) and HOMO-LUMO gap of B-O groups BO_3, BO_4, and B_2O_5.

Groups	P_x, P_y, P_z	Δ*α* (a.u.)	|***β***$_{max}$| (a.u.)	HOMO-LUMO gap (eV)
BO_3	0.0, 0.0, 0.0	7.2	10.9	8.2
BO_4	0.0, 0.0, 0.0	1.0	3.2	10.9
B_2O_5	0.0, 0.2, 0.0	17.5	38.8	8.2

Table S5 Calculated Born effective charges of ternary borates α-/β-$TM_3(BO_3)_2$ (TM = Zn, Cd), $Cd_2B_2O_5$, and $M_3(BO_3)_2$ (M = Hg, Mg, Ca, Sr).

Compounds	Atom	q_{xx}	q_{yy}	q_{zz}	Δq
α-$Zn_3(BO_3)_2$	**Zn**	2.23231	2.13125	2.18877	0.10106
	B	1.84455	1.86249	2.74494	0.90039
	O	−1.73101	−1.68646	−2.00936	−0.32290
β-$Zn_3(BO_3)_2$	**Zn**	2.16634	2.18141	2.29710	0.13076
	B	1.11780	2.77683	2.51281	1.39501
	O	−1.45577	-2.01631	-1.98616	-0.56054
α-$Cd_3(BO_3)_2$	**Cd**	2.46920	2.34877	2.30707	0.16213
	B	0.96846	2.91669	2.48694	1.51848
	O	−1.55742	−2.14662	−1.98252	−0.58920
β-$Cd_3(BO_3)_2$	**Cd**	2.39455	2.31806	2.31894	0.07649
	B	2.30816	1.48933	2.35802	0.86869
	O	−1.96670	−1.65548	−1.94547	−0.31122
$Cd_2B_2O_5$	**Cd**	2.42088	2.28868	2.40227	0.1322□0
	B	1.0401□0	2.98220	2.66980	1.9421□0
	O	−1.38439	−2.10835	−2.02882	−0.72396
$Hg_3(BO_3)_2$	**Hg**	2.15191	2.15196	1.51073	0.64123
	B	2.86827	2.86827	0.57078	2.29749
	O	−2.03205	−2.03207	−0.94563	−1.08644
$Mg_3(BO_3)_2$	**Mg**	2.04758	2.03041	2.13336	0.10295

	B	1.45514	2.31796	2.48557	1.03043
	O	−1.50884	−1.78786	−1.89520	−0.38636
$Ca_3(BO_3)_2$	**Ca**	2.53682	2.53686	2.18309	0.35377
	B	2.66062	2.66063	0.70002	1.96061
	O	−2.15529	−2.14404	−1.32489	−0.83040
$Sr_3(BO_3)_2$	**Sr**	2.60832	2.60828	2.20663	0.40169
	B	2.71211	2.71210	0.56448	2.14763
	O	−2.20820	−2.20817	−1.29147	−0.91673

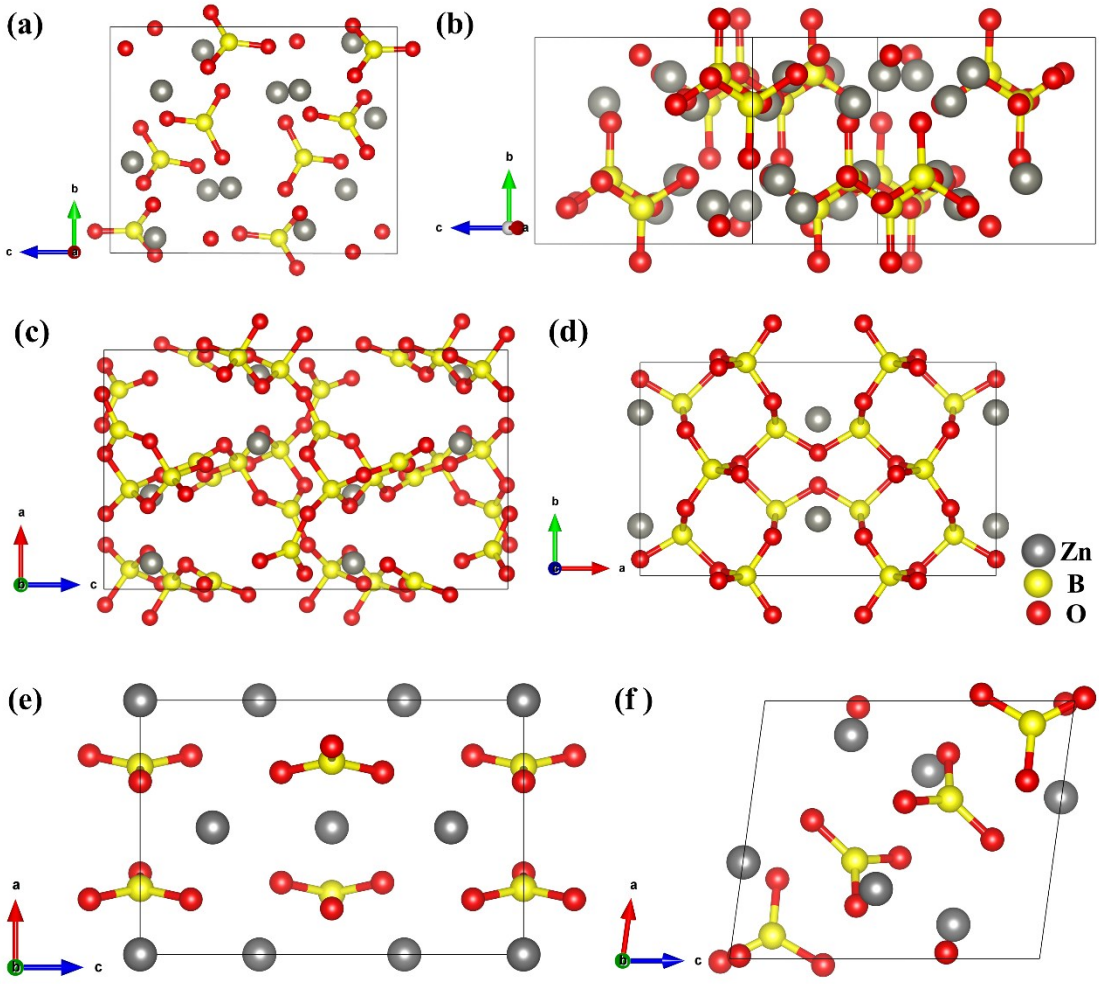
Table S6 Calculated optical permittivity and polarisabilities (*f*–>infinity) of ternary borates α-/β-$TM_3(BO_3)_2$ (TM = Zn, Cd), $Cd_2B_2O_5$, and $M_3(BO_3)_2$ (M = Hg, Mg, Ca, Sr).

Compounds	**Optical Permittivity (*f*-> infinity)**				**Optical Polarisabilities (*f*-> infinity)**			
	ε_{xx}	ε_{yy}	ε_{zz}	$\Delta\varepsilon$	P_{xx}	P_{yy}	P_{zz}	ΔP
α-$Zn_3(BO_3)_2$	3.23	3.15	3.34	0.19	88.64	85.48	92.90	7.42
β-$Zn_3(BO_3)_2$	3.07	3.36	3.39	0.32	161.47	184.69	186.81	25.34
α-$Cd_3(BO_3)_2$	3.42	3.57	3.44	0.15	49.54	52.69	50.03	3.15
β-$Cd_3(BO_3)_2$	3.47	3.29	3.39	0.18	52.45	48.29	50.65	4.16
$Cd_2B_2O_5$	3.04	3.26	3.36	0.32	33.95	37.67	39.25	5.30
$Hg_3(BO_3)_2$	4.10	4.10	3.00	1.10	220.52	220.52	142.17	78.35
$Mg_3(BO_3)_2$	2.74	2.74	2.81	0.07	28.23	28.28	29.41	1.18
$Ca_3(BO_3)_2$	3.22	3.22	2.78	0.44	135.43	135.43	108.68	26.75
$Sr_3(BO_3)_2$	3.17	3.17	2.72	0.45	153.71	153.71	121.93	31.78

Table S7 The BO_3 groups density (N/V) of ternary borates α-/β-$TM_3(BO_3)_2$ (TM = Zn, Cd), $Cd_2B_2O_5$,

and $M_3(BO_3)_2$ (M = Hg, Mg, Ca, Sr).

Compounds	Number of BO_3 in cell (N)	Cell volume (Å^3) (V)	Density of BO_3 groups
α-$Zn_3(BO_3)_2$	8	498.73	1.60×10^{-2}
β-$Zn_3(BO_3)_2$	16	981.67	1.63×10^{-2}
α-$Cd_3(BO_3)_2$	6	257.41	2.33×10^{-2}
β-$Cd_3(BO_3)_2$	4	266.33	1.50×10^{-2}
$Cd_2B_2O_5$	4	209.36	1.91×10^{-2}
$Hg_3(BO_3)_2$	24	894.05	2.68×10^{-2}
$Mg_3(BO_3)_2$	6	204.30	2.94×10^{-2}
$Ca_3(BO_3)_2$	24	765.61	3.13×10^{-2}
$Sr_3(BO_3)_2$	24	889.93	2.70×10^{-2}



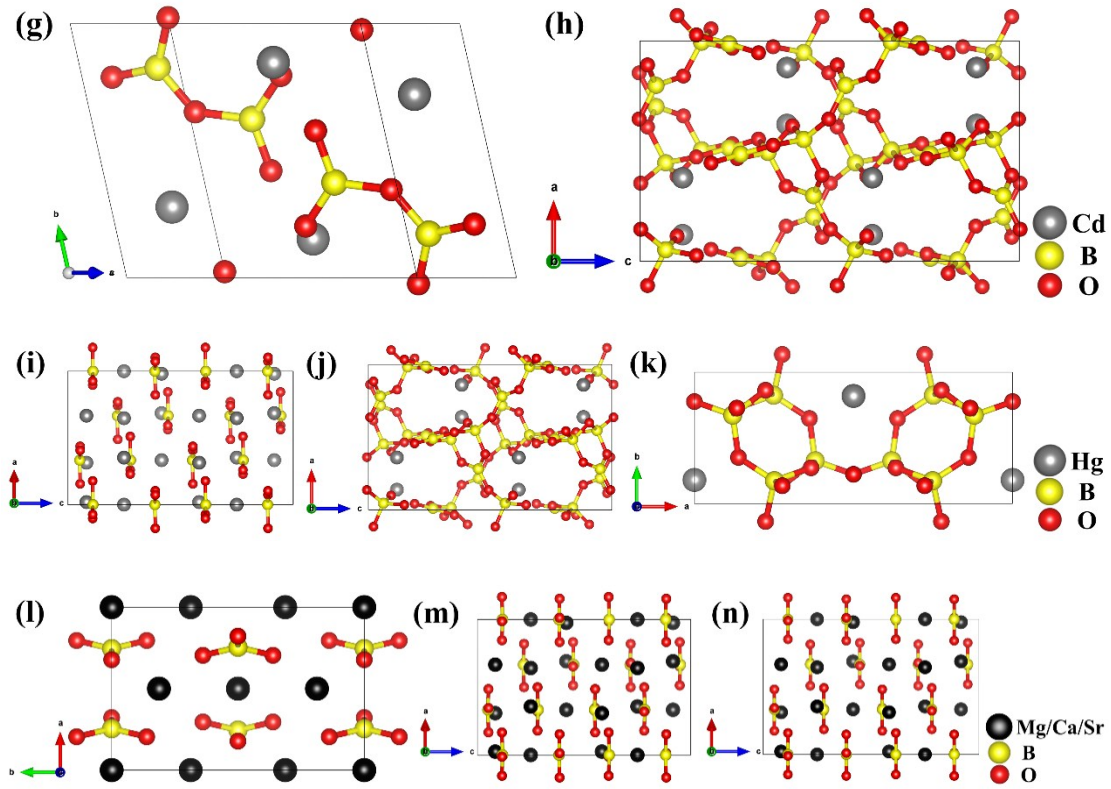
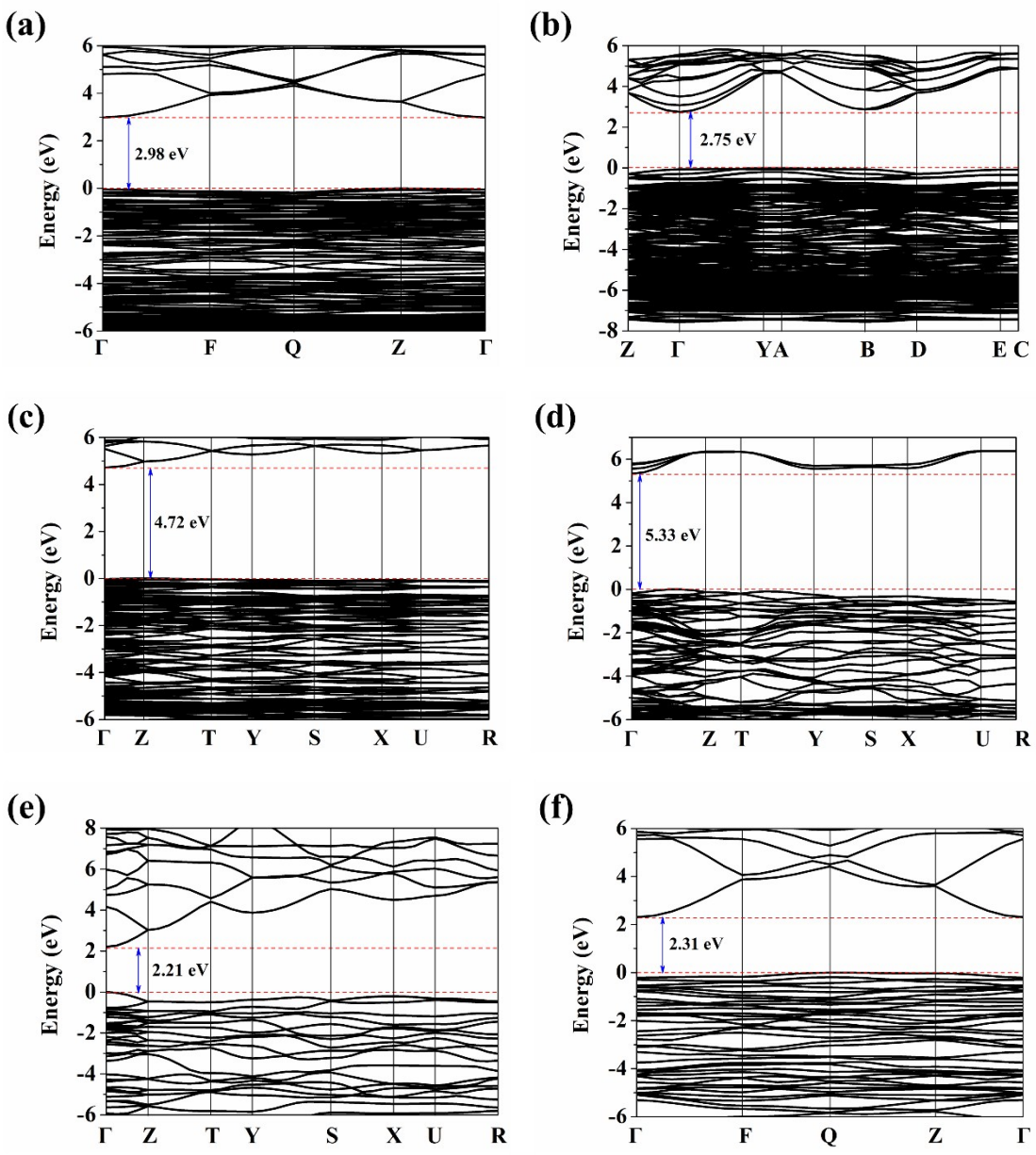


Figure S1 Crystal structures of ternary borates α-$Zn_3(BO_3)_2$ (a), β-$Zn_3(BO_3)_2$ (b), α-ZnB_4O_7 (c), β-ZnB_4O_7 (d), α-$Cd_3(BO_3)_2$ (e), β-$Cd_3(BO_3)_2$ (f), $Cd_2B_2O_5$ (g), CdB_4O_7 (h), $Hg_3(BO_3)_2$ (i), α-HgB_4O_7 (j), β-HgB_4O_7 (k),and $M_3(BO_3)_2$ (M = Mg, Ca, Sr) (l-n).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(b)
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Z Γ YA B D E C
(c)
Energy (eV)
4.72 eV
Γ Z T Y S X U R
(d)
Energy (eV)
5.33 eV
Γ Z T Y S X U R
(e)
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(f)
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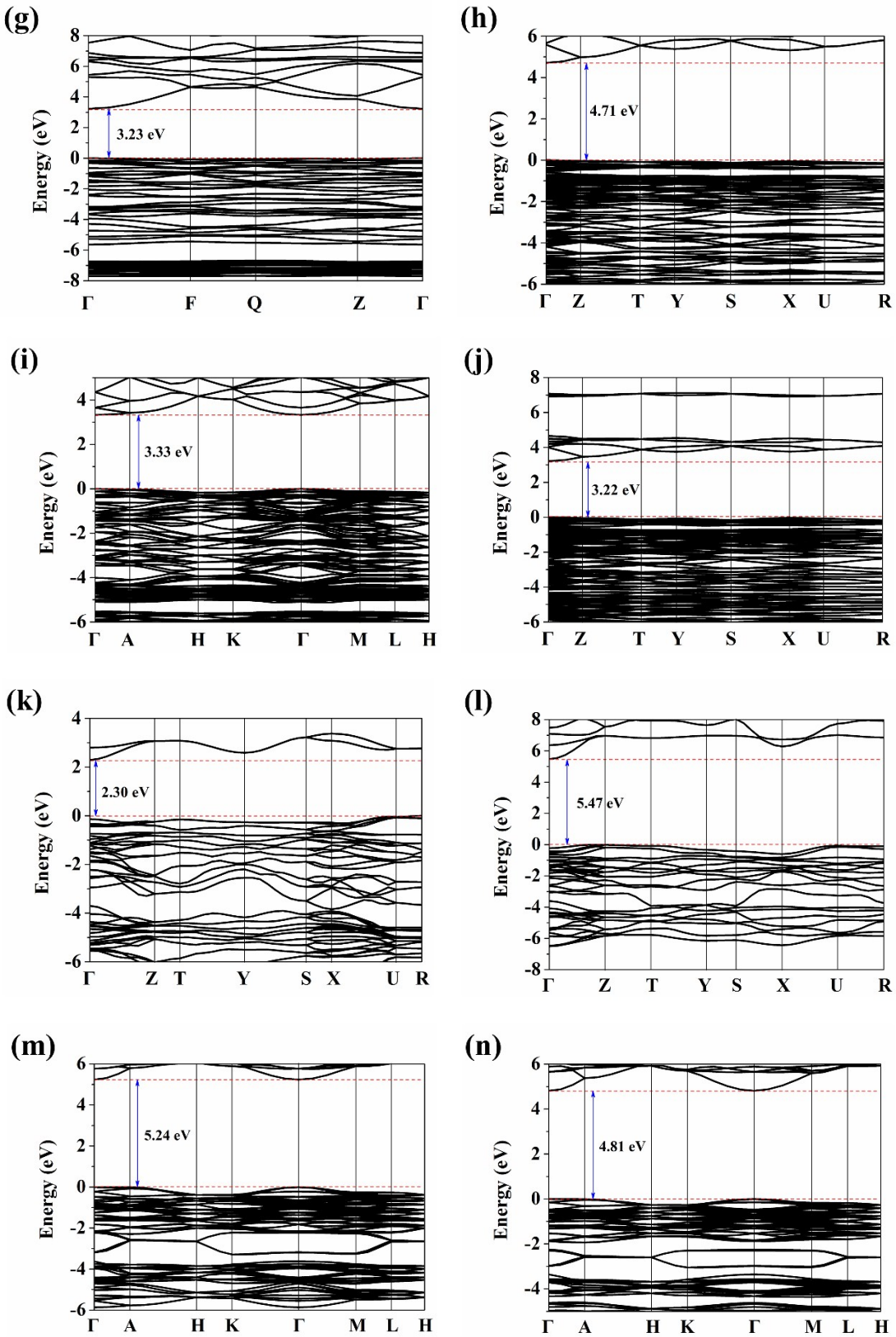
Γ F Q Z Γ


(g)
Energy (eV)
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Γ F Q Z Γ
(h)
Energy (eV)
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(j)
Energy (eV)
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(k)
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(l)
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Γ Z T Y S X U R
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Γ A H K Γ M L H

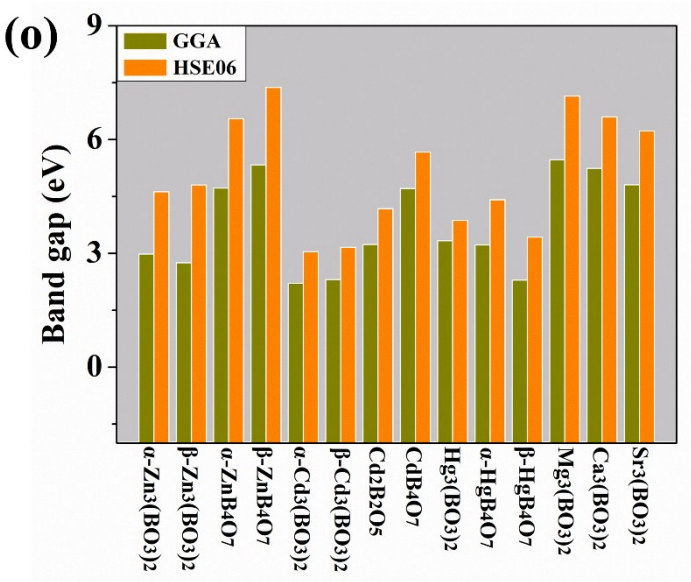
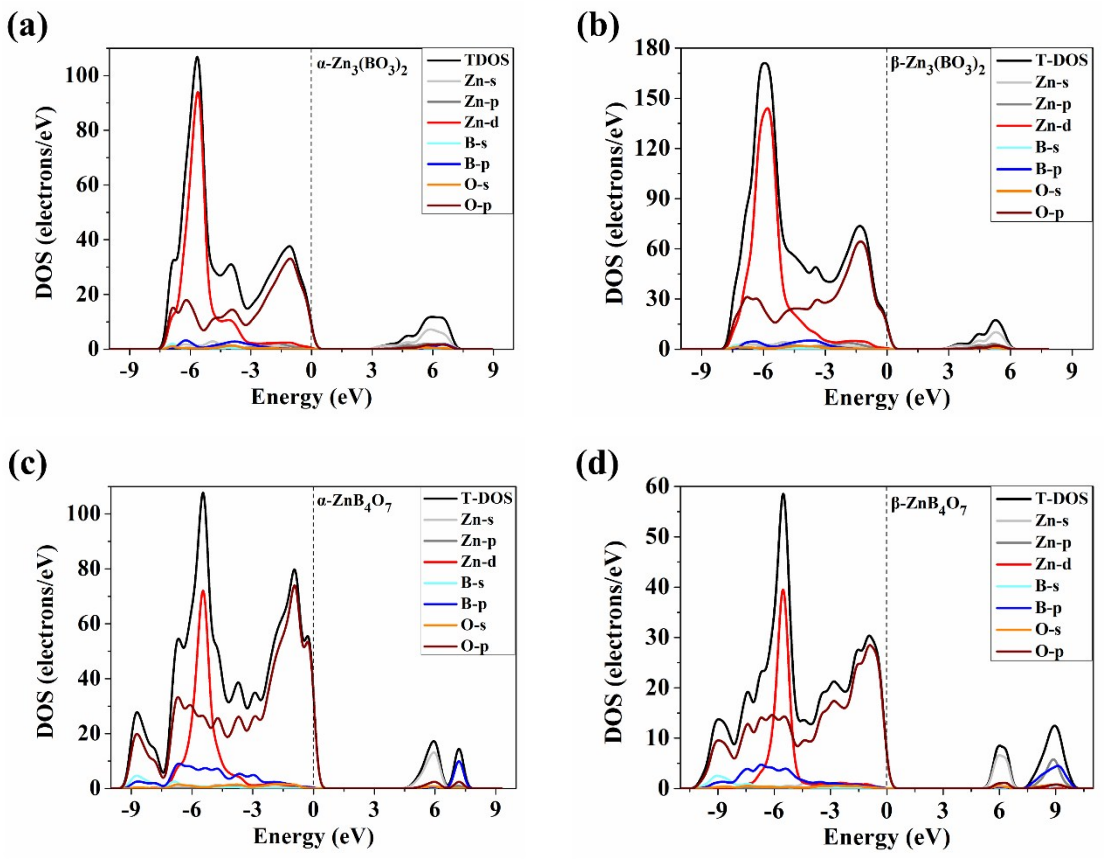
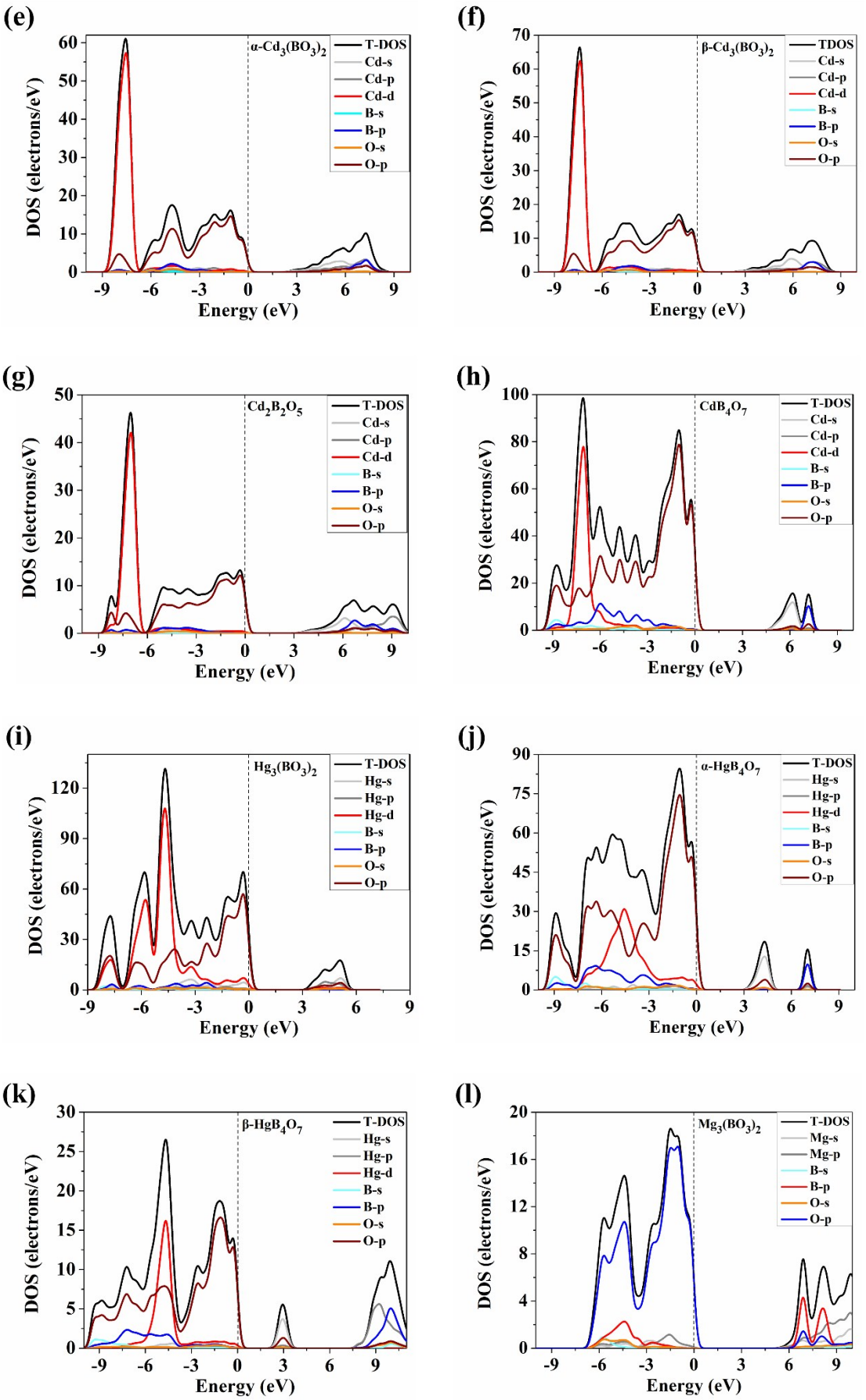


Figure S2 Calculated band structures for ternary borates α-$Zn_3(BO_3)_2$ (a), β-$Zn_3(BO_3)_2$ (b), α-ZnB_4O_7 (c), β-ZnB_4O_7 (d), α-$Cd_3(BO_3)_2$ (e), β-$Cd_3(BO_3)_2$ (f), $Cd_2B_2O_5$ (g), CdB_4O_7 (h), $Hg_3(BO_3)_2$ (i), α-HgB_4O_7 (j), β-HgB_4O_7 (k), and $M_3(BO_3)_2$ (M = Mg, Ca, Sr) (l-n) by GGA functional, all of borates calculated band gaps by the GGA and HSE06 functional (o).


(a)
α-Zn3(BO3)2
TDOS
Zn-s
Zn-p
Zn-d
B-s
B-p
O-s
O-p
DOS (electrons/eV)
Energy (eV)
(b)
β-Zn3(BO3)2
T-DOS
Zn-s
Zn-p
Zn-d
B-s
B-p
O-s
O-p
DOS (electrons/eV)
Energy (eV)
(c)
α-ZnB4O7
T-DOS
Zn-s
Zn-p
Zn-d
B-s
B-p
O-s
O-p
DOS (electrons/eV)
Energy (eV)
(d)
β-ZnB4O7
T-DOS
Zn-s
Zn-p
Zn-d
B-s
B-p
O-s
O-p
DOS (electrons/eV)
Energy (eV)


(e)
α-Cd3(BO3)2
T-DOS
Cd-s
Cd-p
Cd-d
B-s
B-p
O-s
O-p
DOS (electrons/eV)
Energy (eV)
(f)
β-Cd3(BO3)2
TDOS
Cd-s
Cd-p
Cd-d
B-s
B-p
O-s
O-p
DOS (electrons/eV)
Energy (eV)
(g)
Cd2B2O5
T-DOS
Cd-s
Cd-p
Cd-d
B-s
B-p
O-s
O-p
DOS (electrons/eV)
Energy (eV)
(h)
CdB4O7
T-DOS
Cd-s
Cd-p
Cd-d
B-s
B-p
O-s
O-p
DOS (electrons/eV)
Energy (eV)
(i)
Hg3(BO3)2
T-DOS
Hg-s
Hg-p
Hg-d
B-s
B-p
O-s
O-p
DOS (electrons/eV)
Energy (eV)
(j)
α-HgB4O7
T-DOS
Hg-s
Hg-p
Hg-d
B-s
B-p
O-s
O-p
DOS (electrons/eV)
Energy (eV)
(k)
β-HgB4O7
T-DOS
Hg-s
Hg-p
Hg-d
B-s
B-p
O-s
O-p
DOS (electrons/eV)
Energy (eV)
(l)
Mg3(BO3)2
T-DOS
Mg-s
Mg-p
B-s
B-p
O-s
O-p
DOS (electrons/eV)
Energy (eV)

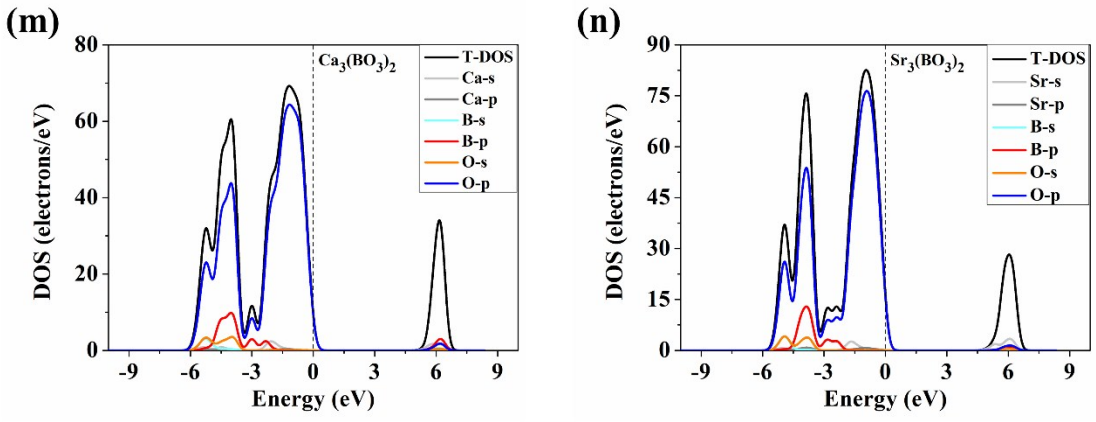


Figure S3 Density/partial density of states of ternary borates α-$Zn_3(BO_3)_2$ (a), β-$Zn_3(BO_3)_2$ (b), α-ZnB_4O_7 (c), β-ZnB_4O_7 (d), α-$Cd_3(BO_3)_2$ (e), β-$Cd_3(BO_3)_2$ (f), $Cd_2B_2O_5$ (g), CdB_4O_7 (h), $Hg_3(BO_3)_2$ (i), α-HgB_4O_7 (j), β-HgB_4O_7 (k),and $M_3(BO_3)_2$ (M = Mg, Ca, Sr) (l-n).

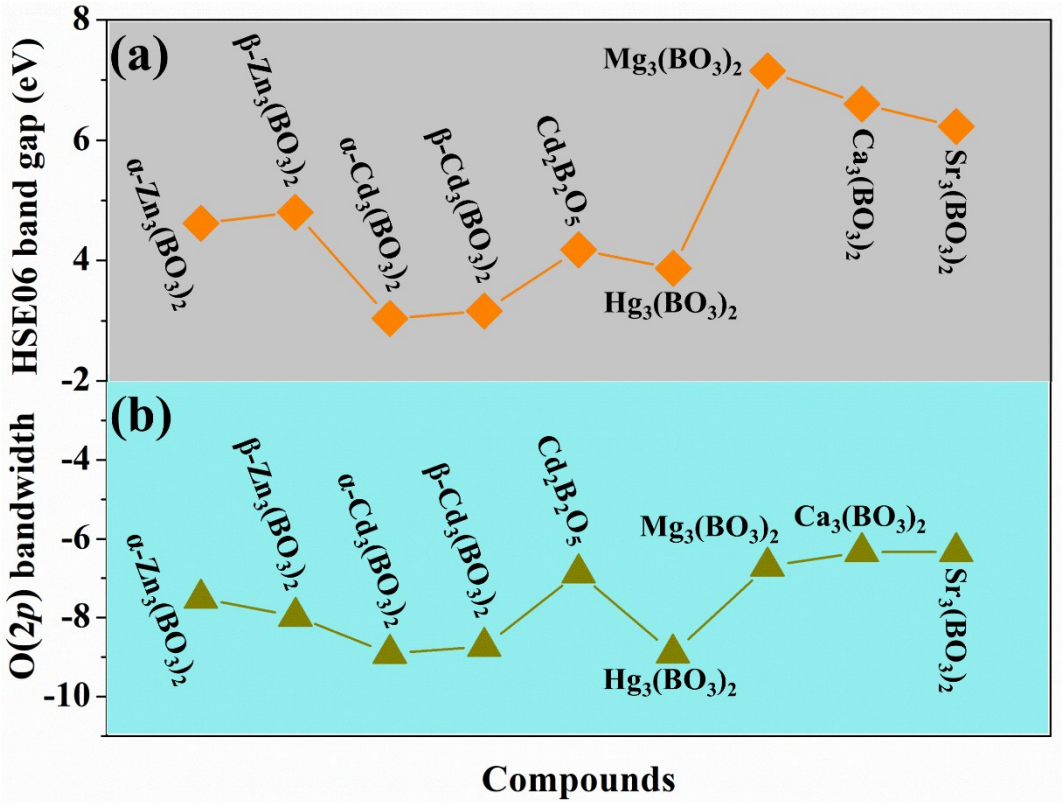
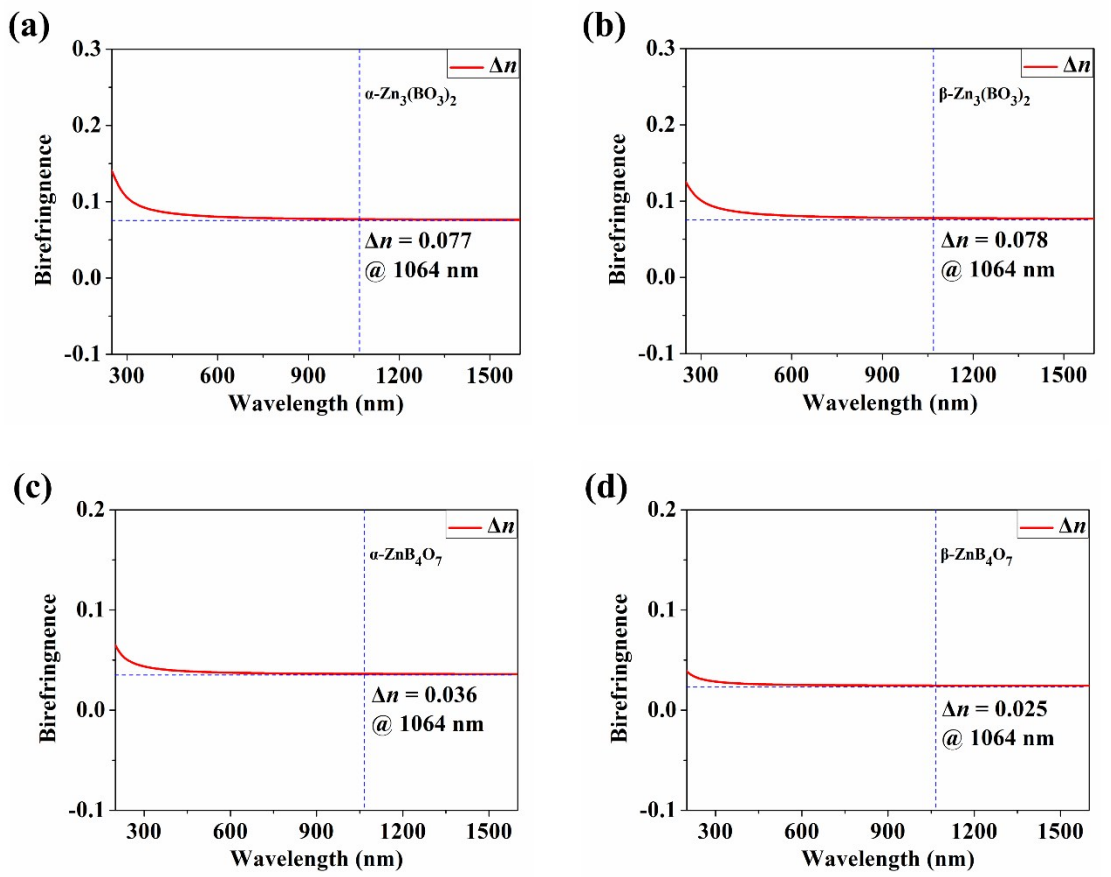
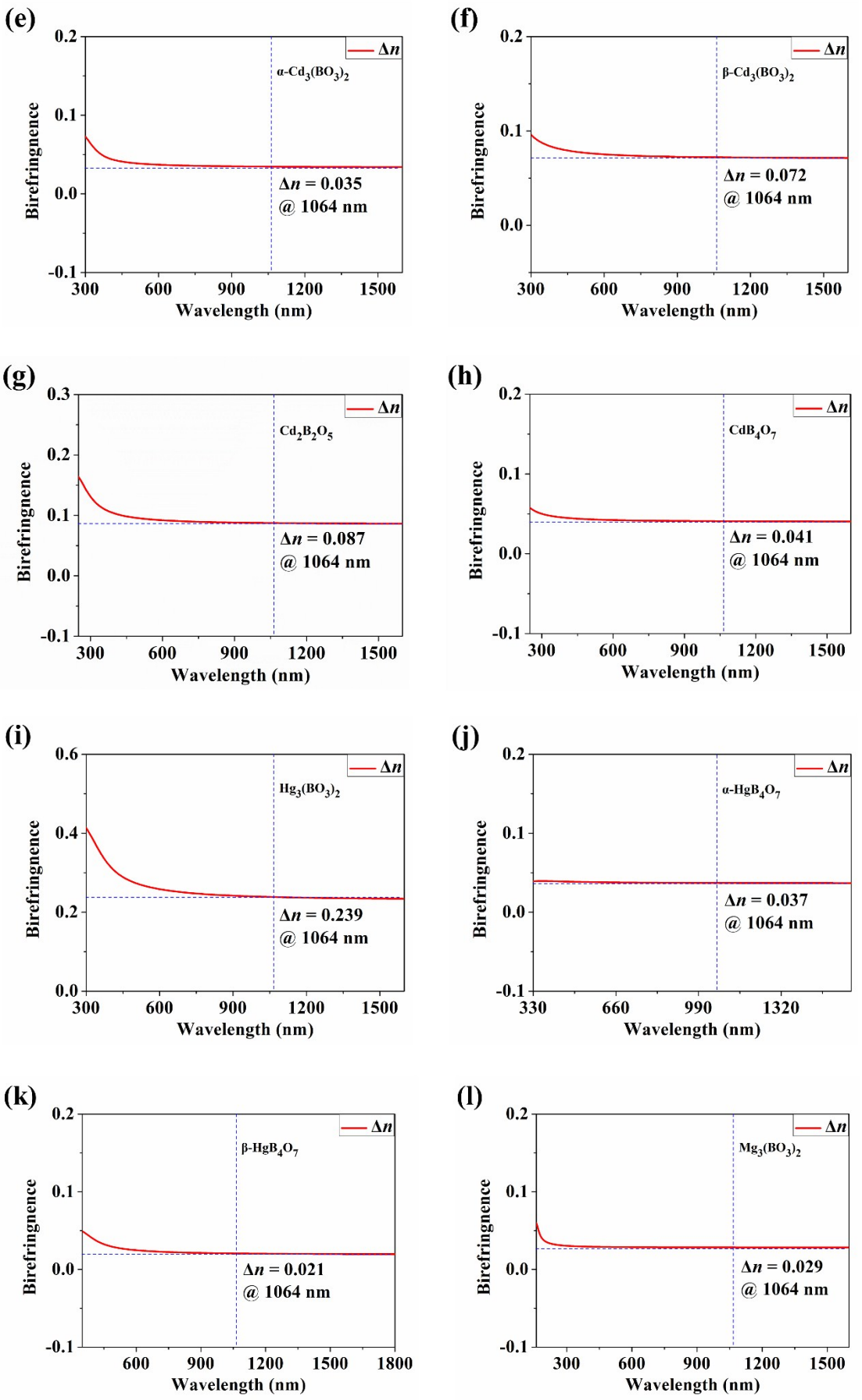


Figure S4 Ternary borates α-/β-$TM_3(BO_3)_2$ (TM = Zn, Cd), $Cd_2B_2O_5$, and $M_3(BO_3)_2$ (M = Hg, Mg, Ca,

Sr): compared with the HSE06 band gaps (a) and O (2*p*) bandwidth (b).




(e)
α-Cd3(BO3)2
Δn = 0.035
@ 1064 nm
(f)
β-Cd3(BO3)2
Δn = 0.072
@ 1064 nm
(g)
Cd2B2O5
Δn = 0.087
@ 1064 nm
(h)
CdB4O7
Δn = 0.041
@ 1064 nm
(i)
Hg3(BO3)2
Δn = 0.239
@ 1064 nm
(j)
α-HgB4O7
Δn = 0.037
@ 1064 nm
(k)
β-HgB4O7
Δn = 0.021
@ 1064 nm
(l)
Mg3(BO3)2
Δn = 0.029
@ 1064 nm
Δn
Birefringence
Wavelength (nm)

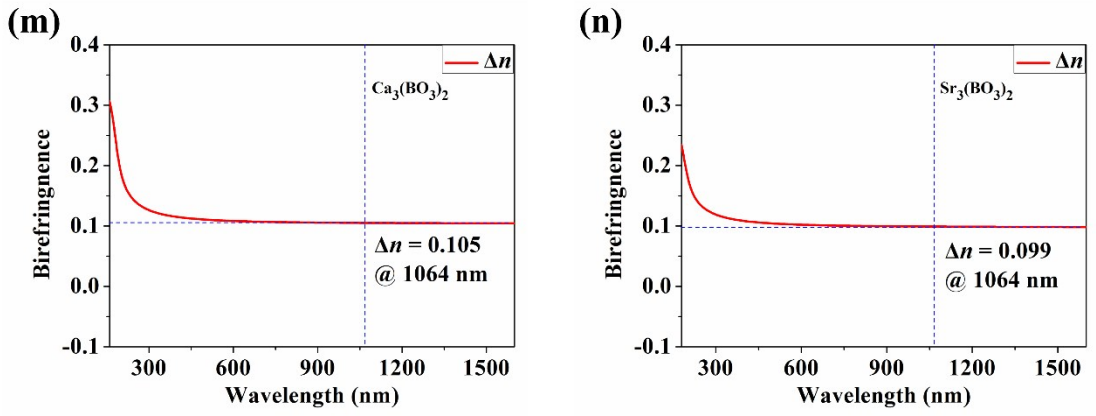


Figure S5 Calculated birefringence Δn of ternary borates α-$Zn_3(BO_3)_2$ (a), β-$Zn_3(BO_3)_2$ (b), α-ZnB_4O_7 (c), β-ZnB_4O_7 (d), α-$Cd_3(BO_3)_2$ (e), β-$Cd_3(BO_3)_2$ (f), $Cd_2B_2O_5$ (g), CdB_4O_7 (h), $Hg_3(BO_3)_2$ (i), α-HgB_4O_7 (j), β-HgB_4O_7 (k), and $M_3(BO_3)_2$ (M = Mg, Ca, Sr) (l-n).

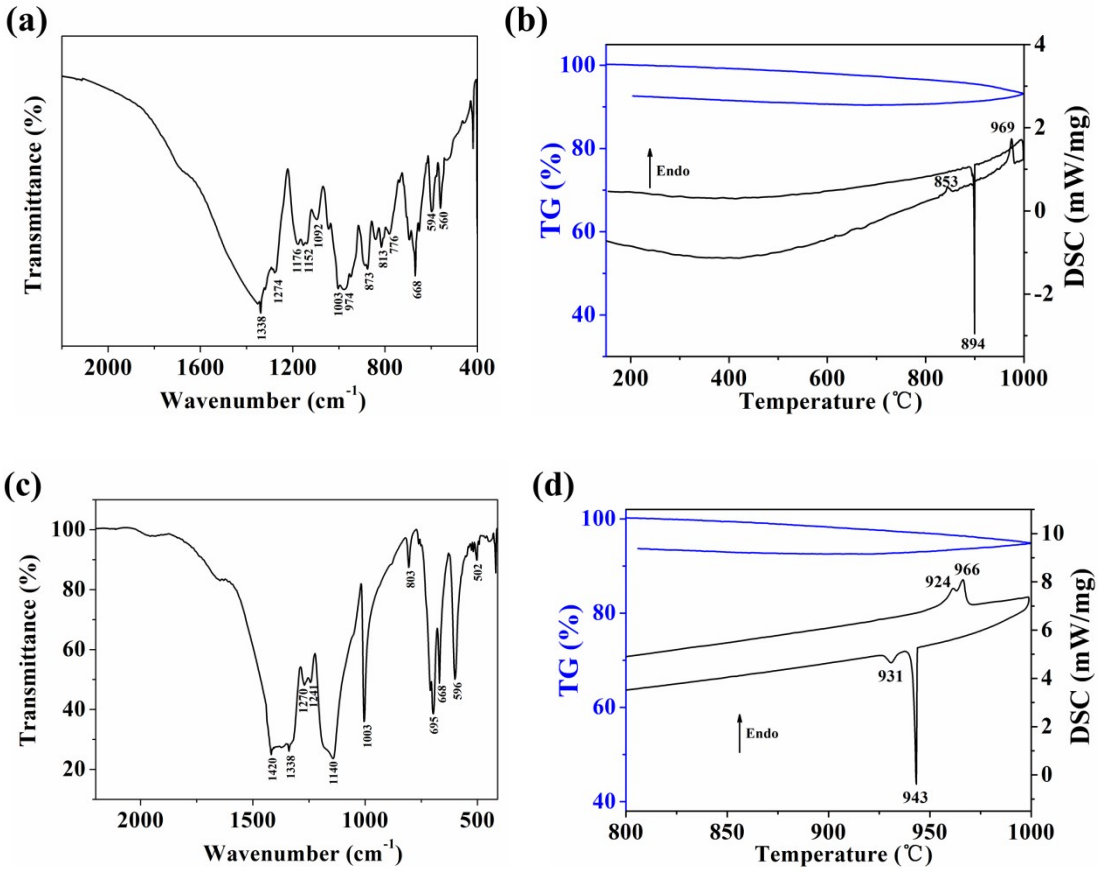


Figure S6 Borates α-$Cd_3(BO_3)_2$ and $Cd_2B_2O_5$: IR spectra and thermal analysis. (a) and (b) are IR and thermal of α-$Cd_3(BO_3)_2$, (c) and (d) are those of $Cd_2B_2O_5$.

To further determine the coordination of B atoms of α-$Cd_3B_2O_6$, the IR spectrum is measured within range of wavenumber from 400 to 4000 cm^{-1} (Figure S6a) and the polycrystalline samples were mixed

with dried KBr in a molar ratio of 1:100 approximately. According to Figure S6a, the strong peaks at the range of 1338 to 1003 cm^{-1} are ascribed to antisymmetric stretch of BO_3 groups while other peaks below 974 cm^{-1} mainly from the bending mode of BO_3 units. The results are in accordance with other compounds containing BO_3 anionic groups. In order to evaluate the thermal stability of α-$Cd_3B_2O_6$, thermal gravimetric (TG) analysis and differential scanning calorimetry (DSC) data are collected at the temperature range of 40 to 1000 °C. The TGA and DSC curves of α-$Cd_3B_2O_6$ are shown in the Figure S6b, and blue line is the TG curve. It can be seen there is a weight loss about 5% in the heating and cooling process. This loss may attribute to the decomposition of boron at high temperature. Black line represents the DSC curve, and it shows two endothermic peaks at 853 and 969 °C in the heating process, and one exothermic peak at around 894 °C in the cooling process.

The IR spectrum of $Cd_2B_2O_5$ depicts in Figure S6c, and the peaks from 1420 to 1241 cm^{-1} and 1140 to 1003 cm^{-1} can be assigned to the asymmetric and symmetric stretching vibrations of the BO_3 groups, respectively. The peaks below 803 cm^{-1} are caused by the distortion modes. The Figure S6d reveals the TG and DSC curves. The blue line is TG curve, and there are about 5% weight loss in the process of heating and cooling. The black line represents the DSC curve, and there is one endothermic peak at 966 °C in the heating curve and two exothermic peaks at 943 and 931 °C in the cooling curve.

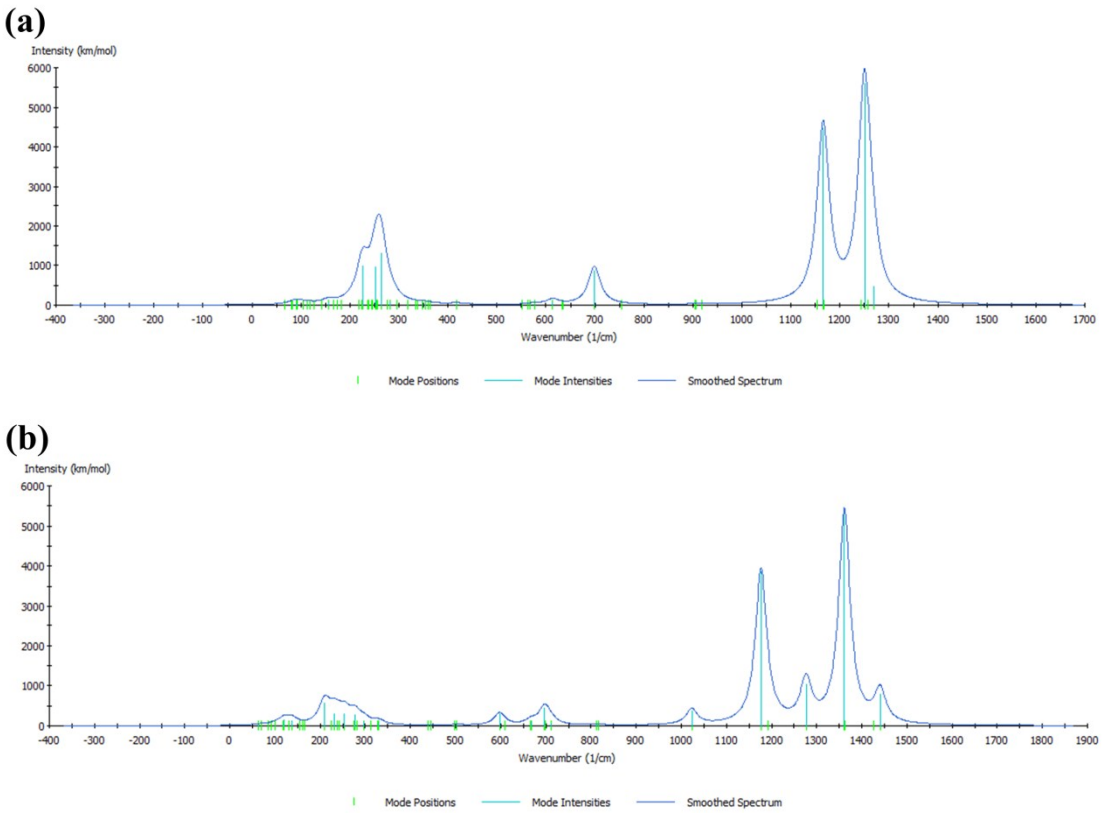


Figure S7 Calculated IR spectra of α-$Cd_3(BO_3)_2$ (a) and $Cd_2B_2O_5$ (b).

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