Supporting Information

A new polymorph $Cd_3B_2O_6$: synthesis, crystal structure and phase transformation

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Table S1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for β-$Cd_3B_2O_6$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor. BVS is the calculated bond valence sum in β-$Cd_3B_2O_6$.

Atom	x	y	z	U(eq)	BVS
Cd1	7295(1)	650(1)	5590(1)	9(1)	2.08
Cd2	3739(1)	7604(1)	19(1)	10(1)	1.93
Cd3	1323(1)	4430(1)	7067(1)	10(1)	1.95
B1	3804(6)	4335(6)	3605(5)	10(1)	2.90
B2	9108(6)	-1672(6)	8731(5)	10(1)	2.92
O1	3917(4)	2427(4)	5039(3)	11(1)	1.93
O2	5375(4)	4704(4)	2052(3)	11(1)	1.99
O3	6911(4)	-729(4)	8815(3)	11(1)	2.04
O4	2053(4)	5973(4)	3849(3)	11(1)	1.90
O5	10115(4)	-2565(4)	10291(3)	13(1)	1.98
O6	10244(4)	-1710(4)	6961(3)	13(1)	1.93

Table S2. Anisotropic displacement parameters ($Å^2 \times 10^3$) for β-$Cd_3B_2O_6$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cd1	9(1)	9(1)	9(1)	-1(1)	-1(1)	-1(1)
Cd2	9(1)	10(1)	12(1)	-4(1)	0(1)	-1(1)
Cd3	9(1)	12(1)	8(1)	-1(1)	0(1)	-2(1)
B1	11(2)	11(2)	9(2)	-4(1)	-2(1)	-4(1)
B2	11(2)	8(2)	11(2)	-2(1)	1(1)	-2(1)
O1	11(1)	10(1)	12(1)	0(1)	-3(1)	-2(1)
O2	11(1)	12(1)	9(1)	-4(1)	0(1)	-1(1)
O3	9(1)	12(1)	12(1)	-3(1)	0(1)	-2(1)
O4	11(1)	10(1)	13(1)	-4(1)	-2(1)	-1(1)
O5	12(1)	19(1)	9(1)	1(1)	-3(1)	-4(1)
O6	12(1)	15(1)	10(1)	-2(1)	0(1)	3(1)

Table S3. Selected bond lengths (Å) and angles (deg.) for β-Cd$_3$B$_2$O$_6$.

Atom Contact	Lengths/Angles	Atom Contact	Lengths/Angles
Cd1-O1	2.257(2)	Cd3-O2#3	2.378(2)
Cd1-O1#2	2.288(2)	Cd3-O4	2.349(2)
Cd1-O3	2.330(2)	Cd3-O4#8	2.333(2)
Cd1-O4#3	2.306(2)	Cd3-O5#7	2.143(2)
Cd1-O6	2.367(2)	Cd3-O6#9	2.364(2)
Cd1-O6#1	2.244(2)	B1-O1	1.391(4)
Cd2-O2	2.284(2)	B1-O2	1.371(4)
Cd2-O2#6	2.284(2)	B1-O4	1.390(4)
Cd2-O3#3	2.250(2)	B2-O3	1.389(4)
Cd2-O3#5	2.268(2)	B2-O5	1.366(4)
Cd2-O5#4	2.206(2)	B2-O6	1.388(4)
Cd3-O1	2.424(2)		
O1-Cd1-O1#2	86.38(9)	O3#3-Cd2-O5#4	89.41(9)
O1-Cd1-O3	104.48(8)	O3#5-Cd2-O5#4	152.89(9)
O1-Cd1-O4#3	84.34(8)	O1-Cd3-O2#3	83.54(8)
O1-Cd1-O6	163.76(9)	O1-Cd3-O4	59.43(8)
O1-Cd1-O6#1	108.33(8)	O1-Cd3-O4#8	100.74(8)
O1#2-Cd1-O3	94.65(8)	O1-Cd3-O5#7	118.47(9)
O1#2-Cd1-O4#3	170.71(8)	O1-Cd3-O6#9	133.12(8)
O1#2-Cd1-O6	89.16(8)	O2#3-Cd3-O4	97.78(8)
O1#2-Cd1-O6#1	101.49(9)	O2#3-Cd3-O4#8	173.31(8)
O3-Cd1-O4#3	87.32(8)	O2#3-Cd3-O5#7	99.61(9)
O3-Cd1-O6	60.31(8)	O2#3-Cd3-O6#9	82.64(8)
O3-Cd1-O6#1	144.09(8)	O4-Cd3-O4#8	80.24(9)
O4#3-Cd1-O6	99.67(9)	O4-Cd3-O5#7	162.09(9)
O4#3-Cd1-O6#1	81.85(9)	O4-Cd3-O6#9	78.47(8)
O6-Cd1-O6#1	87.86(9)	O4#8-Cd3-O5#7	82.94(9)
O2-Cd2-O2#6	84.95(9)	O4#8-Cd3-O6#9	90.70(8)
O2-Cd2-O3#3	110.64(9)	O5#7-Cd3-O6#9	107.94(9)
O2-Cd2-O3#5	95.51(8)	O1-B1-O2	123.4(3)
O2-Cd2-O5#4	111.52(8)	O1-B1-O4	116.7(3)
O2#6-Cd2-O3#3	161.09(9)	O2-B1-O4	119.8(3)
O2#6-Cd2-O3#5	89.43(9)	O3-B2-O5	122.7(3)
O2#6-Cd2-O5#4	94.80(9)	O3-B2-O6	116.4(3)
O3#3-Cd2-O3#5	78.76(9)	O5-B2-O6	120.9(3)

Note. Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y,-z+1   #2 -x+1,-y,-z+1   #3 -x+1,-y+1,-z+1

#4 x-1,y+1,z-1   #5 x,y+1,z-1   #6 -x+1,-y+1,-z

#7 -x+1,-y,-z+2   #8 -x,-y+1,-z+1   #9 x-1,y+1,z

#10 x,y-1,z+1   #11 x+1,y-1,z+1   #12 x+1,y-1,z

Table S4. Magnitude of the SOJT distortion of the CdO_6 octahedra in α-$Cd_3B_2O_6$ and CdO_n (n = 5, 6) polyhedra in β- $Cd_3B_2O_6$.

compd.	species	dipole moment				
					magnitude	
		$x(a)$	$y(b)$	$z(c)$	debye	$\times 10^{-4}$ esu·cm/ $Å^3$
α	$Cd1O_6$	0	0	0	0	0
	$Cd2O_6$	0	0	1.7097	1.7097	132.84
β	$Cd1O_6$	1.4311	-0.4057	1.9625	2.5389	190.65
	$Cd2O_5$	1.7214	-0.6944	0.5371	1.8826	141.37
	$Cd3O_6$	-0.2781	2.2089	-3.1907	3.4606	259.87

Figure S1 The linked styles of each Cd1 octahedron, Cd2 hexahedron, Cd3 octahedron, B1 planar and B2 planar group with other CdO_n (n = 5, 6) distorted polyhedra in β-$Cd_3B_2O_6$.
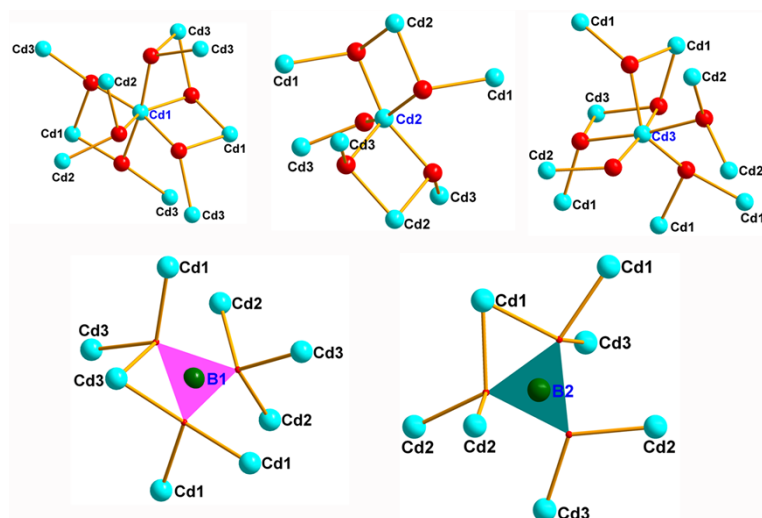
Figure S2 The IR spectra of α-Cd$_3$B$_2$O$_6$ (a) and β-Cd$_3$B$_2$O$_6$ (b).

(a)

(b)