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Electronic Supplementary Information

$Li_6Zn_3(BO_3)_4$: A New Zincoborate Featuring Vertex-, Edge- and Face-sharing LiO_4 Tetrahedra Configuration with Reversible Phase Transitions

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Table S1. Atomic coordinates, equivalent isotropic displacement parameters and bond valence sum (BVS) for $Li_6Zn_3(BO_3)_4$

Atoms	Wyckoff positions	*x*	*y*	*z*	U(eq)	BVS
Li(1)	*2i*	7630(20)	958(12)	650(10)	10(2)	1.032
Li(2)	*2i*	7870(30)	3876(15)	5435(13)	28(3)	0.946
Li(3)	*2i*	12920(20)	3698(11)	8238(9)	5(2)	1.052
Li(4)	*2i*	8740(20)	5330(12)	8144(10)	11(2)	1.035
Li(5)	*2i*	3800(30)	-1473(17)	5829(12)	25(3)	1.053
Li(6)	*2i*	2640(30)	767(13)	7772(12)	20(3)	1.035
Zn(1)	*2i*	1430(2)	2769(1)	3473(1)	13(1)	1.963
Zn(2)	*2i*	3445(2)	2682(1)	546(1)	11(1)	2.016
Zn(3)	*2i*	7550(2)	787(1)	6904(1)	13(1)	2.002
B(1)	*2i*	-2104(17)	3050(8)	-667(7)	12(2)	2.992
B(2)	*2i*	6879(16)	4120(8)	3031(6)	9(1)	2.944
B(3)	*2i*	2161(16)	2058(8)	5698(7)	10(2)	2.990
B(4)	*2i*	7216(17)	-552(8)	8145(7)	14(2)	2.931
O(1)	*2i*	-495(9)	2821(5)	317(4)	10(1)	1.969
O(2)	*2i*	5694(9)	41(5)	7375(4)	11(1)	2.073
O(3)	*2i*	-189(10)	4385(5)	3179(4)	11(1)	2.073
O(4)	*2i*	3818(10)	825(5)	920(4)	12(1)	1.958
O(5)	*2i*	1344(10)	1819(5)	6677(4)	12(1)	2.003
O(6)	*2i*	299(10)	2363(5)	4845(4)	15(1)	2.001
O(7)	*2i*	4997(10)	2836(5)	-772(4)	13(1)	2.059
O(8)	*2i*	5237(9)	4445(5)	2105(4)	11(1)	1.914
O(9)	*2i*	9084(10)	3500(5)	8499(4)	12(1)	2.014
O(10)	*2i*	4882(10)	2040(5)	5602(4)	14(1)	1.986
O(11)	*2i*	5657(10)	3522(6)	3807(4)	16(1)	1.943
O(12)	*2i*	297(9)	849(5)	2032(4)	10(1)	1.994

Table S2. Selected bond lengths (Å) and angles (deg) for $Li_6Zn_3(BO_3)_4$

Zn(1)-O(6)	1.938(5)	Li(5)-O(10)$^{\#3}$	1.944(14)
Zn(1)-O(11)	1.955(5)	Li(5)-O(11)$^{\#3}$	2.165(15)
Zn(1)-O(3)	1.972(4)	Li(6)-O(2)	1.905(13)
Zn(1)-O(12)	2.008(5)	Li(6)-O(12)$^{\#1}$	1.935(12)
Zn(2)-O(7)	1.912(5)	Li(6)-O(5)	1.944(13)
Zn(2)-O(1)	1.956(4)	Li(6)-O(7)$^{\#13}$	2.114(14)
Zn(2)-O(4)	1.969(4)	B(1)-O(9)$^{\#5}$	1.364(9)
Zn(2)-O(8)	1.998(5)	B(1)-O(7)$^{\#4}$	1.374(9)
Zn(3)-O(10)	1.931(5)	B(1)-O(1)	1.378(9)
Zn(3)-O(5)$^{\#9}$	1.947(5)	B(2)-O(11)	1.374(9)
Zn(3)-O(2)	1.965(4)	B(2)-O(3)$^{\#9}$	1.376(9)
Zn(3)-O(9)	2.001(5)	B(2)-O(8)	1.384(8)
Li(1)-O(12)$^{\#9}$	1.935(12)	B(3)-O(6)	1.368(9)
Li(1)-O(4)	1.958(12)	B(3)-O(5)	1.369(9)
Li(1)-O(1)$^{\#9}$	1.964(11)	B(3)-O(10)	1.380(9)
Li(1)-O(4)$^{\#8}$	2.016(12)	B(4)-O(12)$^{\#3}$	1.373(9)
Li(2)-O(3)$^{\#2}$	1.902(15)	B(4)-O(4)$^{\#3}$	1.378(9)
Li(2)-O(11)	1.923(15)	B(4)-O(2)	1.388(9)
Li(2)-O(10)	2.074(14)	O(9)$^{\#5}$-B(1)-O(7)$^{\#4}$	120.3(6)
Li(2)-O(6)$^{\#9}$	2.158(14)	O(9)$^{\#5}$-B(1)-O(1)	122.7(6)
Li(3)-O(7)$^{\#11}$	1.886(11)	O(7)$^{\#4}$-B(1)-O(1)	117.0(6)
Li(3)-O(9)	1.958(11)	O(11)-B(2)-O(3)$^{\#9}$	118.7(6)
Li(3)-O(8)$^{\#7}$	1.961(11)	O(11)-B(2)-O(8)	121.8(6)
Li(3)-O(5)$^{\#9}$	2.054(11)	O(3)$^{\#9}$-B(2)-O(8)	119.5(6)
Li(4)-O(3)$^{\#2}$	1.919(12)	O(6)-B(3)-O(5)	119.4(6)
Li(4)-O(9)	1.931(11)	O(6)-B(3)-O(10)	120.8(6)
Li(4)-O(8)$^{\#2}$	2.001(12)	O(5)-B(3)-O(10)	119.7(6)
Li(4)-O(1)$^{\#2}$	2.024(12)	O(12)$^{\#3}$-B(4)-O(4)$^{\#3}$	121.4(6)
Li(5)-O(2)	1.890(14)	O(12)$^{\#3}$-B(4)-O(2)	119.9(6)
Li(5)-O(6)$^{\#1}$	1.900(13)	O(4)$^{\#3}$-B(4)-O(2)	118.6(6)

Symmetry transformations used to generate equivalent atoms:#1-x,-y,-z+1 #2 -x+1,-y+1,-z+1 #3 -x+1,-y,-z+1 #4 x-1,y,z #5 x-1,y,z-1 #7 -x+2,-y+1,-z+1 #8 -x+1,-y,-z #9 x+1,y,z #11 x+1,y,z+1 #13 x,y,z+1

Table S3. The basic information of the existing anhydrous and disorder-free lithium - containing borates

NO.	Chemical formula	Li-O units	Li-O configuration	Dimension of Li-O structure	B-O configuration	ICSD number
1	$LiGd_6O_5(BO_3)_3$	LiO_3	Isolated	0D	Isolated BO_3	50685
2	$LiY_6O_5(BO_3)_3$	LiO_3	Isolated	0D	Isolated BO_3	160603
3	$Sr_2Li(BeB_3O_8)$	LiO_3	Isolated	0D	Isolated BO_3+ Isolated B_2O_5	262730
4	$SrLi(B_9O_{15})$	LiO_3	Isolated	0D	BO_3+BO_4 network	93015
5	$LiBaB_9O_{15}$	LiO_3	Isolated	0D	BO_3+BO_4 network	426537/ 183692
6	$Rb_2LiNd(BO_3)_2$	LiO_4	Isolated	0D	Isolated BO_3	430190
7	$Cs_2LiNd(BO_3)_2$	LiO_4	Isolated	0D	Isolated BO_3	429483
8	$LiB(GeO_4)$	LiO_4	Isolated	0D	Isolated BO_4	67535/ 28106
9	$Li(B(SO_4)_2)$	LiO_4	Isolated	0D	Isolated BO_4	425174
10	$Li(AlB_2O_5)$	LiO_4	Isolated	0D	Isolated B_2O_5	51314
11	$Li_2Pb_2(CuB_4O_{10})$	LiO_4	Isolated	0D	Isolated B_2O_5	180108
12	$Li_2(AlB_5O_{10})$	LiO_4	Isolated	0D	Isolated B_5O_{10}	279578
13	$LiBa_2(B_5O_{10})$	LiO_4	Isolated	0D	BO_3+BO_4 chain	71875
14	$Li_3B_{11}O_{18}$	LiO_4	Isolated	0D	BO_3+BO_4 network	427426
15	$Li(B_3O_5)$	LiO_4	Isolated	0D	BO_3+BO_4 network	84617
16	$Li_2O(B_2O_3)_3$	LiO_4	Isolated	0D	BO_3+BO_4 network	38206
17	$Li_3(B_7O_{12})$	LiO_4	Isolated	0D	BO_3+BO_4 network	68475
18	$Li_2Sr_4B_{12}O_{23}$	LiO_4	Isolated	0D	BO_3+BO_4 network	424308
19	$CsLi(B_6O_{10})$	LiO_4	Isolated	0D	BO_3+BO_4 network	427396/ 427409
20	$K_2Ba_4Ga_4Li_2B_6O_{21}$	LiO_4	Vertex-sharing	0D	Isolated BO_3	291378
21	$RbLi_2Ga_2(BO_3)_3$	LiO_4	Vertex-sharing	0D	Isolated BO_3	280205
22	$Li_3NaBaB_6O_{12}$	LiO_4	Vertex-sharing	0D	Isolated $B_{12}O_{24}$	423774
23	$LiK(B_4O_7)$	LiO_4	Vertex-sharing	0D	BO_3+BO_4 network	280296
24	$LiNaB_4O_7$	LiO_4	Vertex-sharing	0D	BO_3+BO_4 network	416956

25	$LiRb(B_4O_7)$	LiO_4	Vertex-sharing	0D	BO_3+BO_4 network	280297
26	$LiMn(BO_3)$	LiO_4	Vertex-sharing	1D	Isolated BO_3	94318
27	$LiBUO_5$	LiO_4	Vertex-sharing	1D	Isolated BO_3	67114
28	$LiCd(BO_3)$	LiO_4	Vertex-sharing	1D	Isolated BO_3	20835
29	$Li_3Ca_9(BO_3)_7(LiF)_2$	LiO_4	Vertex-sharing	1D	Isolated BO_3	250860
30	$Cs_3Na(Li_2(BO_3)_2)$	LiO_4	Vertex-sharing	1D	Isolated BO_3	36531
31	$Li_2(B_4O_7)$	LiO_4	Vertex-sharing	1D	BO_3+BO_4 network	300010
32	$Li_3Pr_2(BO_3)_3$	LiO_4	Vertex-sharing	2D	Isolated BO_3	20217
33	$LiBO_2$	LiO_4	Vertex-sharing	3D	BO_4 network	34256
34	$Li_3Sc(BO_3)_2$	LiO_4	Vertex-sharing	3D	Isolated BO_3	241234
35	$LiBe(BO_3)$	LiO_4	edge-sharing	0D	Isolated BO_3	427287
36	$LiCd(BO_3)$	LiO_4	edge-sharing	0D	Isolated BO_3	200615
37	$K_9Li_3Nd_3(BO_3)_7$	LiO_4	edge-sharing	0D	Isolated BO_3	429855
38	Li_3BO_3	LiO_4	edge-sharing	3D	Isolated BO_3	9105
39	$CsLi_5(BO_3)_2$	LiO_4	edge-sharing	3D	Isolated BO_3	61203
40	$LiZnBO_3$	LiO_4	Vertex-, edge-sharing	0D	Isolated BO_3	/
41	$Li_6CuB_4O_{10}$	LiO_4	Vertex-, edge-sharing	1D	Isolated B_2O_5	237526
42	$Li_6(Al_2(BO_3)_4)$	LiO_4	Vertex-, edge-sharing	1D	Isolated BO_3	20434
43	$Li_3Gd(BO_3)_2$	LiO_4	Vertex-, edge-sharing	1D	Isolated BO_3	94356
44	K_2LiBO_3	LiO_4	Vertex-, edge-sharing	2D	Isolated BO_3	60949
45	$Li_2(BAlO_4)$	LiO_4	Vertex-, edge-sharing	2D	Isolated BO_3	50612
46	$Li_3(AlB_2O_6)$	LiO_4	Vertex-, edge-sharing	2D	Isolated BO_3	54858
47	$Na_4Li_5(BO_3)_3$	LiO_4	Vertex-, edge-sharing	2D	Isolated BO_3	61204
48	$Li_5(B(SO_4)_4)$	LiO_4	Vertex-, edge-sharing	2D	Isolated BO_4	428002
49	$Li_6CuB_4O_{10}$	LiO_4	Vertex-, edge-sharing	2D	Isolated B_2O_5	247217
50	$LiBO_2$	LiO_4	Vertex-, edge-sharing	2D	BO_3 chain	37060
51	$KLi_2(BO_3)$	LiO_4	Vertex-, edge-sharing	3D	Isolated BO_3	48177
52	$Li_8Be_5B_6O_{18}$	LiO_4	Vertex-, edge-sharing	3D	Isolated BO_3	/

53	$Li_6CuB_4O_{10}$	LiO_4	Vertex-, edge-sharing	3D	Isolated B_2O_5	249215
54	$Li_4Cs_3(B_7O_{14})$	LiO_4	Vertex-, edge-sharing	3D	Isolated B_7O_{14}	261420
55	$Li_2SeB_8O_{15}$	LiO_4	Isolated, vertex-sharing	OD	BO_3+BO_4 network	424079
56	$Li_5Cs_2B_7O_{14}$	LiO_4	Isolated, vertex-, edge-sharing	1D	BO_3+BO_4 chain	251863
57	$Li_5Rb_2(B_7O_{14})$	LiO_4	Isolated, vertex-, edge-sharing	1D	BO_3+BO_4 chain	187060
58	$Li_6Be_3B_4O_{12}$	LiO_4	Vertex-, edge-, face-sharing	3D	Isolated BO_3	/
59	$Li_6Zn_3B_4O_{12}$	LiO_4	Vertex-, edge-, face-sharing	3D	Isolated BO_3	This work
60	$(Li_2((SO_2)_8)(B_{12}Cl)_{12})$	LiO_5	Isolated	0D	disordered	168500
61	$Sr_2LiIn(B_2O_5)_2$	LiO_5	Isolated	0D	Isolated B_2O_5	72486
62	$Sr_2ScLi(B_4O_{10})$	LiO_5	Isolated	0D	Isolated B_2O_5	68429
63	$CsLi_2Gd_4(BO_3)_5$	LiO_5	Vertex-sharing	1D	Isolated BO_3	240894
64	$Li_2Cu_9B_{12}O_{28}$	LiO_5	Vertex-sharing	1D	Isolated B_2O_5 +Isolated B_4O_9	237525
65	$LiCa(BO_3)$	LiO_5	Vertex-sharing	2D	Isolated BO_3	99386
66	$LiBa(BO_3)$	LiO_5	Vertex-, edge-sharing	2D	Isolated BO_3	92843
67	$LiSr(BO_3)$	LiO_5	Vertex-, edge-sharing	2D	Isolated BO_3	92842
68	$Nd_6Li(BO_3)_3O_4F_2$	LiO_6	Isolated	0D	Isolated BO_3	260791
69	$Li(B(S_2O_7)_2)$	LiO_6	Isolated	0D	Isolated BO_4	425175
70	$Li(B(SO_3Cl)_4)$	LiO_6	Isolated	0D	Isolated BO_4	16486
71	$LiSrTb_2(BO_3)_3$	LiO_6	Isolated	0D	disordered	196283
72	$LiSrY_2(BO_3)_3$	LiO_6	Isolated	0D	disordered	422091
73	$Li(Co_{0.95}B_{0.05}O_2)$	LiO_6	edge-sharing	2D	disordered	77880
74	$Li_4Cs(B_5O_{10})$	LiO_4+ LiO_5	Vertex-, edge-sharing	0D	Isolated B_5O_{10}	251864
75	LiB_3O_5	LiO_4+ LiO_5	Vertex-, edge-sharing	0D	BO_3+BO_4 network	422922
76	$Li_3CuB_3O_7$	LiO_4+ LiO_5	Vertex-, edge-sharing	1D	IsolatedB_2O_5+ Isolated B_3O_7	237524
77	$Li_8Cu_7B_{14}O_{32}$	LiO_4+ LiO_5	Vertex-, edge-sharing	1D	Isolated B_2O_5+ Isolated B_5O_{11}	237527
78	$Li_3Cs_2(B_5O_{10})$	LiO_4+	Vertex-, edge-	2D	Isolated B_5O_{10}	180730

		LiO_5	sharing			
79	$Li_6Rb_5(B_{11}O_{22})$	LiO_4+ LiO_5	Vertex-, edge-sharing	2D	Isolated $B_{11}O_{22}$	183434
80	$Li_4CaB_2O_6$	LiO_4+ LiO_5	Vertex-, edge-sharing	3D	Isolated BO_3	239000
81	$NaLi_2BO_3$	LiO_4+ LiO_5	Vertex-, edge-sharing	3D	Isolated BO_3	62532
82	$Li_3In(B_2O_6)$	LiO_4+ LiO_5	Vertex-, edge-sharing	3D	Isolated BO_3	94355
83	$Li_6Gd(BO_3)_3$	LiO_4+ LiO_5	Vertex-, edge-sharing	3D	Isolated BO_3	96123
84	$Li_6Ho(BO_3)_3$	LiO_4+ LiO_5	Vertex-, edge-sharing	3D	Isolated BO_3	2121
85	$Li_6Yb(BO_3)_3$	LiO_4+ LiO_5	Vertex-, edge-sharing	3D	Isolated BO_3	200079
86	$Li_6Y(BO_3)_3$	LiO_4+ LiO_5	Vertex-, edge-sharing	3D	Isolated BO_3	68653
87	$Li_6Nd(BO_3)_3$	LiO_4+ LiO_5	Vertex-, edge-sharing	3D	Isolated BO_3	164145
88	$Li_6B_4O_9$	LiO_4+ LiO_5	Vertex-, edge-sharing	3D	Isolated B_4O_9	427421
89	$Li_6Ga_2(BO_3)_4$	LiO_4+ LiO_6	Vertex-, edge-sharing	2D	Isolated BO_3	9987
90	$Li_3Nd_2(BO_3)_3$	LiO_3+ LiO_4	Vertex-sharing	1D	Isolated BO_3	200078
91	$Li_2Yb_5O_4(BO_3)_3$	LiO_3+ LiO_5	Vertex-, edge-sharing	1D	Isolated BO_3	51442
92	$Li_{14}Be_5B(BO_3)_9$	LiO_{3+} LiO_4+ LiO_6	Vertex-, edge-sharing	3D	Isolated BO_3	67991

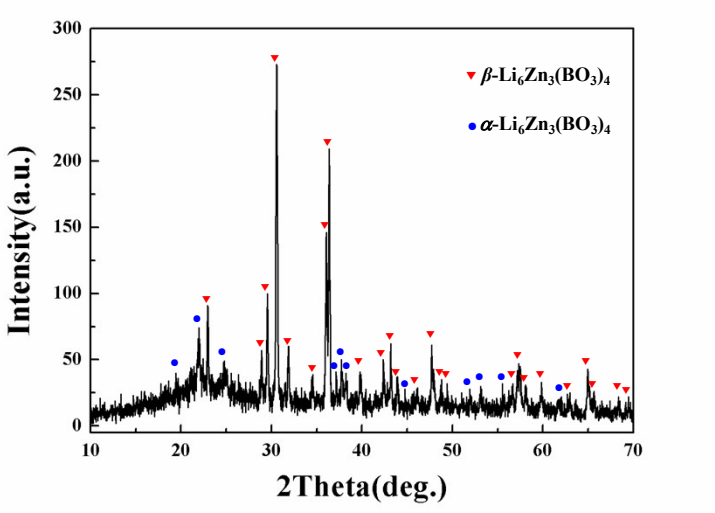

Fig. S1. The PXRD pattern of $Li_6Zn_3(BO_3)_4$ obtained by quenching method using liquid nitrogen at 400 °C.

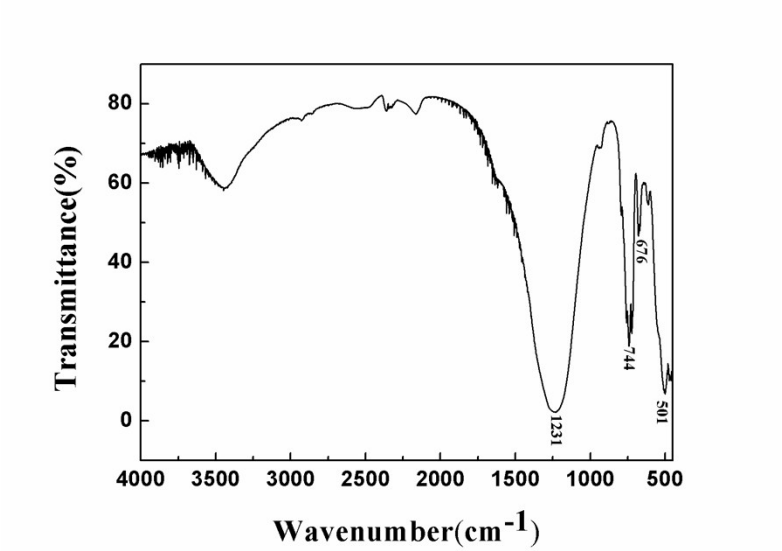

Fig. S2. IR spectrum of $Li_6Zn_3(BO_3)_4$.

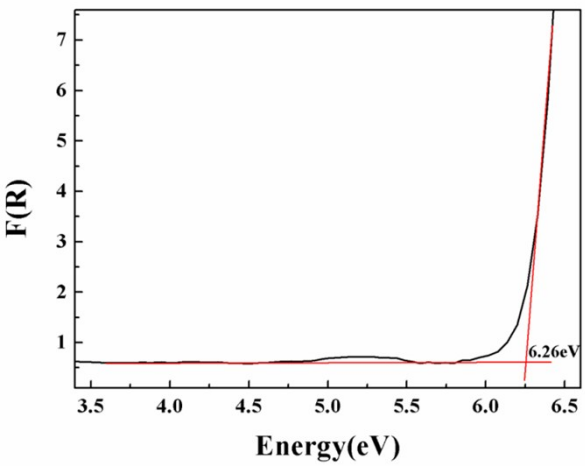

Fig. S3. Absorption spectrum for $Li_6Zn_3(BO_3)_4$.

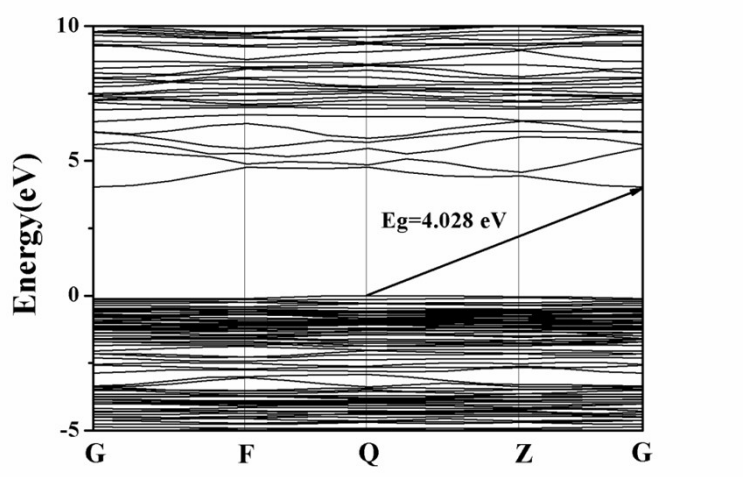

Fig. S4. Calculated band structure of $Li_6Zn_3(BO_3)_4$.