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$Ba_2ZnSc(BO_3)_3$ and $Ba_4Zn_5Sc_2(BO_3)_8$: First Examples of Borates in Zn-Sc-B-O System Featuring Special Structure Configurations

Yanna Chen,‡[a,b] Min Zhang,‡[a] Cong Hu,[a,b] Zhihua Yang[a] and Shilie Pan*[a]

[a] *CAS Key Laboratory of Functional Materials and Devices for Special Environments, Xinjiang Technical Institute of Physics & Chemistry, CAS; Xinjiang Key Laboratory of Electronic Information Materials and Devices, 40-1 South Beijing Road, Urumqi 830011, China.*

[b] *University of Chinese Academy of Sciences, Beijing 100049, China*

E-mail: slpan@ms.xjb.ac.cn

Table S1. Atomic coordinates, equivalent isotropic displacement parameters and bond valence sum (BVS) for $Ba_2ZnSc(BO_3)_3$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atoms	*x*	*y*	*z*	U(eq)	BVS
Ba(1)	0.4483(1)	0.1298(1)	0.2344(1)	0.008(1)	2.084
Ba(2)	0.2592(1)	0.5936(1)	0.2026(1)	0.008(1)	2.116
Zn(1)	0.0952(1)	0.2856(1)	0.4749(1)	0.010(1)	1.829
Sc(1)	-0.1818(1)	-0.1718(1)	0.1556(1)	0.006(1)	2.977
B(1)	-0.2261(8)	0.0214(6)	0.4862(6)	0.007(1)	2.905
B(2)	-0.0524(9)	0.1884(7)	0.1204(6)	0.007(1)	2.958
B(3)	0.3325(9)	0.5326(7)	0.8251(6)	0.008(1)	2.960
O(1)	-0.1928(5)	0.1997(4)	0.5106(3)	0.009(1)	2.034
O(2)	-0.3571(5)	-0.1203(4)	0.3280(4)	0.009(1)	1.989
O(3)	-0.1284(5)	-0.0168(4)	0.6168(4)	0.009(1)	1.784
O(4)	0.1149(5)	0.3110(4)	0.2739(4)	0.011(1)	2.000
O(5)	-0.2211(5)	0.0487(4)	0.1094(4)	0.010(1)	2.124
O(6)	0.1730(5)	0.4238(4)	0.8551(4)	0.008(1)	2.155
O(7)	-0.0433(5)	0.2058(4)	-0.0232(4)	0.011(1)	1.921
O(8)	0.5123(5)	0.6786(4)	0.9568(4)	0.010(1)	1.911
O(9)	0.3299(6)	0.4968(4)	0.6638(4)	0.013(1)	1.911

Table S2. Atomic coordinates, equivalent isotropic displacement parameters and bond valence sum (BVS) for $Ba_4Zn_5Sc_2(BO_3)_8$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atoms	*x*	*y*	*z*	U(eq)	BVS
Ba(1)	0.3456(1)	-0.1091(1)	0.6435(1)	0.010(1)	2.037
Ba(2)	0.8410(1)	0.4009(1)	0.5913(1)	0.010(1)	2.050
Zn(1)	0.4383(1)	0.2746(1)	0.5392(1)	0.012(1)	2.008
Zn(2)	0.2650(1)	0.4651(1)	0.6766(1)	0.011(1)	2.079
Zn(3)	0.8116(1)	0.7359(1)	0.6939(1)	0.017(1)	1.982
Sc(1)	1.0425(1)	0.5101(1)	0.8858(1)	0.020(1)	2.788
B(1)	0.9250(5)	0.1911(6)	0.8184(4)	0.009(1)	2.952
B(2)	0.4705(6)	0.4450(5)	0.3696(4)	0.010(1)	2.965
B(3)	0.6601(6)	0.0513(5)	0.6143(4)	0.011(1)	2.959
B(4)	0.1534(6)	0.2230(5)	0.5525(4)	0.009(1)	2.956
O(1)	0.5234(4)	0.1050(4)	0.6098(3)	0.018(1)	1.916
O(2)	0.4578(4)	0.4336(3)	0.6509(3)	0.010(1)	2.134
O(3)	0.9929(4)	0.6023(3)	0.7265(3)	0.011(1)	2.182
O(4)	0.1721(4)	0.6433(4)	0.6270(3)	0.013(1)	2.038
O(5)	0.1104(4)	0.0857(3)	0.5433(3)	0.012(1)	2.321
O(6)	0.9450(4)	0.3346(3)	0.8094(3)	0.014(1)	2.185
O(7)	0.1340(3)	0.3022(3)	0.6384(3)	0.010(1)	2.050
O(8)	0.2183(3)	0.2868(3)	0.4801(3)	0.010(1)	1.841
O(9)	0.7621(4)	0.1217(3)	0.5749(3)	0.012(1)	2.228
O(10)	0.3008(4)	0.4216(4)	0.8337(3)	0.014(1)	1.906
O(11)	0.6758(4)	0.5726(4)	0.6877(3)	0.012(1)	2.017
O(12)	0.5504(3)	0.3506(4)	0.4468(3)	0.012(1)	1.958

Table S3. Selected bond lengths (Å) and angles (°) for $Ba_2ZnSc(BO_3)_3$.

Ba(1)-O(5)#1	2.727(3)	Sc(1)-O(8)#10	2.066(3)
Ba(1)-O(5)#2	2.750(3	Sc(1)-O(6)#4	2.082(3)
Ba(1)-O(1)#1	2.753(3)	Sc(1)-O(5)	2.089(3)
Ba(1)-O(8)#3	2.793(3)	Sc(1)-O(7)#2	2.090(3)
Ba(1)-O(9)#3	2.811(4)	Sc(1)-O(2)	2.110(3)
Ba(1)-O(4)	2.888(3)	Sc(1)-O(3)#4	2.236(3)
Ba(1)-O(3)#4	2.899(3)	B(1) -O(1)	1.379(6)
Ba(1)-O(2)#1	2.934(3)	B(1) -O(2)	1.379(5)
Ba(1)-O(7)#2	2.962(3)	B(1) -O(3)	1.390(6)
Ba(2)-O(6)#5	2.662(3)	B(2) -O(4)	1.378(6)
Ba(2)-O(2)#6	2.680(3)	B(2) -O(5)	1.366(6)
Ba(2)-O(4)	2.712(3)	B(2) -O(7)	1.384(5)
Ba(2)-O(1)#5	2.726(3)	B(3) -O(6)	1.368(6)
Ba(2)-O(6)#7	2.793(3)	B(3) -O(8)	1.378(6)
Ba(2)-O(7)	2.981(3)	B(3) -O(9)	1.381(5)
Ba(2)-O(9)#3	3.008(4)	O(2)-B(1)-O(1)	118.7(4)
Ba(2)-O(8)#3	3.060(3)	O(2)-B(1)-O(3)	120.1(4)
Ba(2)-O(7)#8	3.066(3)	O(1)-B(1)-O(3)	121.3(4)
Ba(2)-O(8)#7	3.255(3)	O(5)-B(2)-O(4)	120.5(4)
Zn(1)-O(9)	1.923(3)	O(5)-B(2)-O(7)	120.4(4)
Zn(1)-O(4)	1.953(3)	O(4)-B(2)-O(7)	119.0(4)
Zn(1)-O(1)	1.984(3)	O(6)-B(3)-O(8)	120.9(4)
Zn(1)-O(3)#4	2.156(3)	O(6)-B(3)-O(9)	122.3(4)
		O(8)-B(3)-O(9)	116.6(4)

Symmetry transformations used to generate equivalent atoms: #1 x+1,y,z #2 -x,-y,-z #3 -x+1,-y+1,-z+1 #4 -x,-y,-z+1 #5 -x,-y+1,-z+1 #6 x+1,y+1,z #7 x,y,z-1 #8 -x,-y+1,-z #10 x-1,y-1,z-1

Table S4. Selected bond lengths (Å) and angles (°) for $Ba_4Zn_5Sc_2(BO_3)_8$.

Ba(1)-O(9)#1	2.675(3)	Zn(3)-O(6)#9	2.469(4)
Ba(1)-O(1)	2.737(3)	Sc(1)-O(6)	2.007(3)
Ba(1)-O(2)#2	2.754(3)	Sc(1)-O(5)#7	2.034(4)
Ba(1)-O(11)#2	2.814(3)	Sc(1)-O(9)#9	2.039(3)
Ba(1)-O(4)#3	2.826(3)	Sc(1)-O(5)#10	2.128(3)
Ba(1)-O(12)#1	2.862(3)	Sc(1)-O(3)	2.137(3)
Ba(1)-O(5)	2.865(3)	B(1)-O(3)#11	1.373(6)
Ba(1)-O(6)#2	2.994(3)	B(1)-O(4)#2	1.373(6)
Ba(1)-O(10)#2	3.239(4)	B(1)-O(6)	1.384(6)
Ba(2)-O(3)	2.683(3)	B(2)-O(11)#6	1.356(6)
Ba(2)-O(6)	2.740(3)	B(2)-O(12)	1.377(6)
Ba(2)-O(9)	2.741(3)	B(2)-O(2)#6	1.395(6)
Ba(2)-O(11)	2.770(3)	B(3)-O(1)	1.359(6)
Ba(2)-O(7)#5	2.783(3)	B(3)-O(9)	1.374(6)
Ba(2)-O(4)#6	2.789(3)	B(3)-O(10)#2	1.395(6)
Ba(2)-O(12)	2.834(3)	B(4)-O(5)	1.358(6)
Ba(2)-O(8)#6	3.102(3)	B(4)-O(8)	1.385(6)
Zn(1)-O(1)	1.900(3)	B(4)-O(7)	1.386(6)
Zn(1)-O(12)	1.934(3)	O(3)#11-B(1)-O(4)#2	122.9(4)
Zn(1)-O(8)	1.970(3)	O(3)#11-B(1)-O(6)	117.6(4)
Zn(1)-O(2)	2.047(3)	O(4)#2-B(1)-O(6)	119.5(4)
Zn(2)-O(4)	1.921(3)	O(11)#6-B(2)-O(12)	123.5(4)
Zn(2)-O(7)	1.942(3)	O(11)#6-B(2)-O(2)#6	117.6(4)
Zn(2)-O(2)	1.946(3)	O(12)-B(2)-O(2)#6	118.9(4)
Zn(2)-O(10)	1.979(3)	O(1)-B(3)-O(9)	123.1(4)
Zn(3)-O(11)	1.989(4)	O(1)-B(3)-O(10)#2	117.4(4)
Zn(3)-O(10)#7	2.028(3)	O(9)-B(3)-O(10)#2	119.4(4)
Zn(3)-O(3)	2.056(3)	O(5)-B(4)-O(8)	122.6(4)
Zn(3)-O(7)#7	2.145(3)	O(5)-B(4)-O(7)	118.9(4)
Zn(3)-O(8)#6	2.169(3)	O(8)-B(4)-O(7)	118.5(4)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z+1 #2 -x+1,y-1/2,-z+3/2 #3 x,y-1,z #5 x+1,y,z #6 -x+1,-y+1,-z+1 #7 -x+1,y+1/2,-z+3/2 #9 -x+2,y+1/2,-z+3/2 #10 x+1,-y+1/2,z+1/2 #11 -x+2,y-1/2,-z+3/2

Table S5. Basic information of existing anhydrous and disorder-free Zn- or Sc-containing borates.

No.	Structural formula	Space group	B-O units	B-O configuration	Zn/Sc-O units	Zn/Sc-O configuration	Zn/Sc-B-O structure	ICSD Code/ Ref.
1	$Ba_2Zn(BO_3)_2$	$Pca2_1$ (29)	BO_3	isolated (non-coplanar)	ZnO_4	isolated	layer	75606
2	$(BaZn_2B_2O_6)$ $(Ba_2BO_3F)_2$	C12/c1 (15)	BO_3	isolated (non-coplanar)	ZnO_4	isolated	layer	239785
3	$(BaZn_2B_2O_6)$ (Ba_2BO_3F)	Pnma (62)	BO_3	isolated (non-coplanar)	ZnO_4	isolated	network	239784
4	$BaZn_2(BO_3)_2$	$P2_12_12_1$ (19)	BO_3	isolated (non-coplanar)	ZnO_4	vertex-sharing chain	network	72193
5	$Ba_5Zn_4(BO_3)_6$	P1c1 (7)	BO_3	isolated (non-coplanar)	ZnO_4	vertex-sharing isolated (Zn_2O_7)	layer	Ref. a
6	$Ba_2Zn(B_3O_6)_2$	P-1 (2)	BO_3	isolated (B_3O_6) (coplanar)	ZnO_4	edge-sharing isolated (Zn_2O_6)	layer	404486
7	$Ba_3Zn(BO_3)(B_2O_5)F$	$P2_1/c$ (14)	BO_3	isolated (BO_3+B_2O_5) (non-coplanar)	ZnO_4	isolated	layer	Ref. b
8	$Ba_4Zn_2(BO_3)_2(B_2O_5)F_2$	C2/c (15)	BO_3	isolated (BO_3+B_2O_5) (non-coplanar)	ZnO_4	vertex-sharing chain	layer	Ref. b
9	$Zn_3(BO_3)_2$	P-1 (2)	BO_3	isolated (non-coplanar)	ZnO_4	vertex-sharing network	network	155112
10	$Zn_3(BO_3)_2$	C12/c1 (15)	BO_3	isolated (non-coplanar)	ZnO_4	edge-, vertex-sharing network	network	155113
11	$Zn_4O(BO_3)_2$	R-3c (167)	BO_3	isolated (non-coplanar)	ZnO_4	vertex-sharing network	network	72943
12	$PbZn_2(BO_3)_2$	Pccn (56)	BO_3	isolated (non-coplanar)	ZnO_4	vertex-sharing chain	layer	171139
13	$KZn_4(BO_3)_3$	P12/c1 (13)	BO_3	isolated (non-coplanar)	ZnO_4	vertex-sharing layer	network	92615
14	$RbZn_4(BO_3)_3$	P12/c1 (13)	BO_3	isolated (non-coplanar)	ZnO_4	vertex-sharing layer	network	92616
15	$CsZn_4(BO_3)_3$	P12/c1 (13)	BO_3	isolated (non-coplanar)	ZnO_4	vertex-sharing layer	network	250599
16	$Cs_3Zn_6(B_9O_{21})$	$Cmc2_1$ (36)	BO_3	isolated (BO_3+B_3O_6) (non-coplanar)	ZnO_4	vertex-sharing layer	network	194211 / 238088

17	ZnB_4O_7	Cmcm (63)	BO_4	vertex-sharing network	ZnO_5	isolated	network	412688
18	$Zn4O(BO_2)_6$	I-43m (217)	BO_4	vertex-sharing network	ZnO_4	vertex-sharing isolated (Zn_4O_{13})	network	15800
19	$K_3ZnB_5O_{10}$	$P12_1/n1$ (14)	BO_3+BO_4	vertex-sharing isolated (B_5O_{10})	ZnO_4	isolated	layer	262977
20	$Na_3ZnB_5O_{10}$	Pbca (61)	BO_3+BO_4	vertex-sharing isolated (B_5O_{10})	ZnO_4	isolated	layer	423705
21	$Na_3ZnB_5O_{10}$	$P12_1/n1$ (14)	BO_3+BO_4	vertex-sharing isolated (B_5O_{10})	ZnO_4	isolated	layer	417848
22	$Rb_3ZnB_5O_{10}$	$P12_1/n1$ (14)	BO_3+BO_4	vertex-sharing isolated (B_5O_{10})	ZnO_4	isolated	layer	425890
23	$K_2Na(ZnB_5O_{10})$	C12/c1 (15)	BO_3+BO_4	vertex-sharing isolated (B_5O_{10})	ZnO_4	isolated	layer	167139
24	$KZnB_3O_6$	P-1 (2)	BO_3+BO_4	vertex-,edge-sharing isolated (B_6O_{12})	ZnO_4	edge-sharing isolated (Zn_2O_6)	network	421311
25	$Bi_2ZnO(B_2O_6)$	Pba2 (32)	BO_3+BO_4	vertex-sharing isolated (B_2O_5+ B_2O_7)	ZnO_4	isolated	layer	164635
26	$Pb_2Ba_4Zn_4B_{14}O_{31}$	P1 (1)	BO_3+BO_4	vertex-sharing isolated (B_2O_5+ B_6O_{13})	ZnO_4	edge-sharing isolated (ZnO_4+Zn_2O_6)	network	238677
27	$Pb_2Ba_4Zn_4B_{14}O_{31}$	C1c1 (9)	BO_3+BO_4	vertex-sharing isolated (B_2O_5+ B_6O_{13})	ZnO_4	edge-sharing isolated (ZnO_4+Zn_2O_6)	network	238676
28	$Pb_2Ba_4Zn_4B_{14}O_{31}$	$P3_2$ (145)	BO_3+BO_4	vertex-sharing isolated (B_2O_5+ B_6O_{13})	ZnO_4	edge-sharing isolated (ZnO_4+Zn_2O_6)	network	238678
29	$Ba_4K_2Zn_5(B_3O_6)_3$ (B_9O_{19})	$P12_1/n1$ (14)	BO_3+BO_4	vertex-sharing isolated (B_3O_6+ B_8O_{18})	ZnO_4	vertex-sharing isolated (Zn_2O_7+ Zn_3O_{10})	layer	192069
30	$Ba_4Na_2Zn_4(B_3O_6)_2$ ($B_{12}O_{24}$)	P-1 (2)	BO_3+BO_4	vertex-,edge-sharing isolated (B_3O_6+ $B_{12}O_{24}$)	ZnO_4	vertex-sharing isolated (Zn_2O_7)	layer	188636
31	$Ba_2KZn_3(B_3O_6)$ ($O(B_3O_6)_2$)	P-1 (2)	BO_3+BO_4	vertex-sharing isolated	ZnO_4	vertex-, edge-sharing	layer	404485

				(B_3O_6+ B_6O_{13})		isolated (Zn_2O_6+ Zn_2O_7)		
32	$Na_2Zn(B_6O_{11})$	C1c1 (9)	BO_3+BO_4	vertex-sharing layer	ZnO_5	isolated	network	167333
33	$CeZn(B_5O_{10})$	$P12_1/n1$ (14)	BO_3+BO_4	vertex-sharing layer	ZnO_6	edge-sharing isolated (Zn_2O_{10})	network	404537
34	$EuZn(BO_2)_5$	$P12_1/n1$ (14)	BO_3+BO_4	vertex-sharing layer	ZnO_6	edge-sharing isolated (Zn_2O_{10})	network	193587
35	$LaZn(B_5O_{10})$	$P12_1/n1$ (14)	BO_3+BO_4	vertex-sharing layer	ZnO_6	edge-sharing isolated (Zn_2O_{10})	network	248011
36	$NdZn(B_5O_{10})$	$P12_1/n1$ (14)	BO_3+BO_4	vertex-sharing layer	ZnO_6	edge-sharing isolated (Zn_2O_{10})	network	404538
37	$TbZn(B_5O_{10})$	$P12_1/n1$ (14)	BO_3+BO_4	vertex-sharing layer	ZnO_6	edge-sharing isolated (Zn_2O_{10})	network	404539
38	$Pb_4Zn_2B_{10}O_{21}$	Pbcn (60)	BO_3+BO_4	vertex-sharing layer	ZnO_4	isolated	network	250533
39	ZnB_4O_7	Pbca (61)	BO_3+BO_4	vertex-sharing network	ZnO_4	isolated	network	424545
40	$Ba_3Sc(BO_3)_3$	$P6_3cm$ (185)	BO_3	isolated (coplanar)	ScO_6	isolated	layer	75340
41	$KBaSc(BO_3)_2$	R-3m (166)	BO_3	isolated (coplanar)	ScO_6	isolated	layer	252222
42	$BaNaSc(BO_3)_2$	R-3 (148)	BO_3	isolated (coplanar)	ScO_6	isolated	layer	421411
43	$Ba_3ScB_9O_{18}$	$P6_3/m$ (176)	BO_3	Isolated (B_3O_6) (coplanar)	ScO_6	isolated	layer	161090
44	$Ba_2Sc_2(BO_3)_2B_2O_5$	C12/c1 (15)	BO_3	Isolated (BO_3+B_2O_5) (non-coplanar)	ScO_6	isolated + edge-sharing chain	network	86436
45	$Sc(BO_3)$	R-3c (167)	BO_3	isolated (coplanar)	ScO_6	vertex-sharing network	network	195099
46	$CeSc_3(BO_3)_4$	R32 (155)	BO_3	isolated (coplanar)	ScO_6	edge-sharing chain	network	90839
47	$LaSc_3(BO_3)_4$	R32 (155)	BO_3	isolated (coplanar)	ScO_6	edge-sharing chain	network	150812
48	$LaSc_3(BO_3)_4$	C12/c1 (15)	BO_3	isolated (coplanar)	ScO_6	edge-sharing chain	network	83404

49	$PrSc_3(BO_3)_4$	C12/c1 (15)	BO_3	isolated (coplanar)	ScO_6	edge-sharing chain	network	91568
50	$Li_3Sc(BO_3)_2$	$P12_1/c1$ (14)	BO_3	isolated (non-coplanar)	ScO_6	isolated	network	261256
51	$Na_3Sc(BO_3)_2$	$P12_1/c1$ (14)	BO_3	isolated (non-coplanar)	ScO_6	isolated	network	262733
52	$Na_3Sc_2(BO_3)_3$	R-3c (167)	BO_3	isolated (non-coplanar)	ScO_6	face-sharing isolated (Sc_2O_9)	network	245063
53	$Sr_3Sc(BO_3)_3$	R-3 (148)	BO_3	isolated (non-coplanar)	ScO_6	isolated	chain	75339
54	$Sr_6YSc(BO_3)_6$	R-3 (148)	BO_3	isolated (non-coplanar)	ScO_6	isolated	isolated ($Sc_1B_6O_{18}$)	67648
55	$NaSc(B_2O_5)$	$P12_1/c1$ (14)	BO_3	isolated (B_2O_5) (non-coplanar)	ScO_6	edge-sharing chain	network	409522
56	$Sr_2ScLi(B_4O_{10})$	$P12_1/n1$ (14)	BO_3	isolated (B_2O_5) (non-coplanar)	ScO_6	isolated	layer	68429
57	$Sr_2Sc_2(BO_3)_2B_2O_5$	P -1 (2)	BO_3	isolated (BO_3+B_2O_5) (coplanar)	ScO_6	edge-sharing isolated (Sc_2O_{10})	network	86435
58	$Sc_3B_5O_{12}$	Pmna (53)	BO_4	vertex-sharing layer	ScO_8	edge-sharing layer	network	421030
59	$Ba_2ZnSc(BO_3)_3$	P -1 (2)	BO_3	isolated (non-coplanar)	ZnO_4	isolated	Zn-B-O cluster; Zn-Sc-B-O layer	This work
					ScO_6	isolated		
60	$Ba_4Zn_5Sc_2(BO_3)_8$	$P2_1/c$ (14)	BO_3	isolated (non-coplanar)	ZnO_4+ ZnO_6	vertex-, edge-sharing chain	network	This work
					ScO_5	edge-sharing isolated (Sc_2O_8)		

[a]. M. H. Duan, M. J. Xia and R.K. Li, *Inorg. Chem.*, 2017, **56**, 11458.

[b]. M. Mutailipu, X. Su, M. Zhang, Z. H. Yang and S. L. Pan, *Inorg. Chem. Front.*, 2017, **4**, 281.

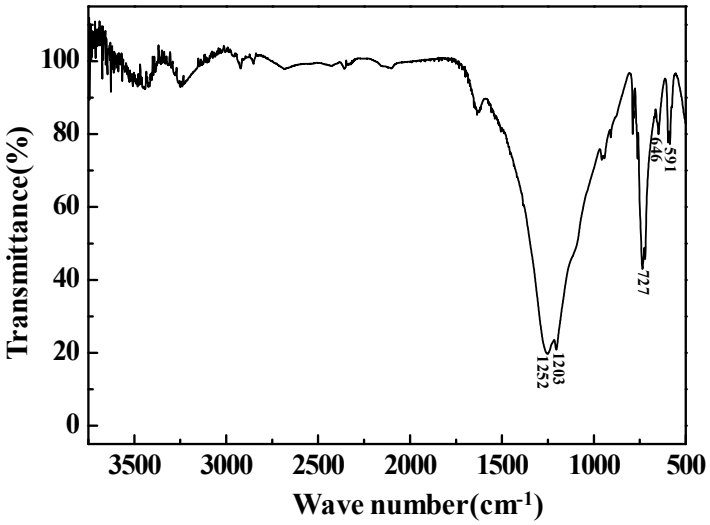

Figure S1. IR spectrum of $Ba_2ZnSc(BO_3)_3$.

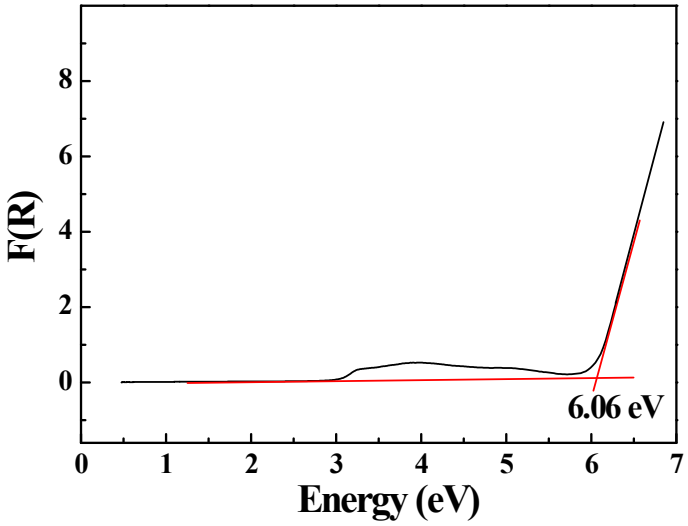

Figure S2. Absorption spectrum of $Ba_2ZnSc(BO_3)_3$.