Supporting Information

$BaLiZn_3(BO_3)_3$: A New Member of $KBe_2BO_3F_2$ Family Possessing the Dense BO_3 Triangles and Smallest Interlayer Distance

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1. Experimental

1.1 Single Crystal Preparation and Polycrystalline Synthesis

Reagents. All the reagents including Li_2CO_3 (Tianjin Baishi Chemical Reagent Co., Ltd., 99.5%), LiF (Aladdin, 99.99%), $BaCO_3$ (Tianjin Baishi Chemical Reagent Co., Ltd., 99.5%), BaF_2 (Shanghai Aladdin Bio-Chem Technology Co., Ltd., 99.99%), ZnO (Aladdin, 99.99%) and H_3BO_3 (Tianjin Baishi Chemical Reagent Co., Ltd., 99.5%) are analytical grade from commercial sources without further purification.

Single Crystal Preparation. Single crystal of $BaLiZn_3(BO_3)_3$ was prepared by high-temperature solution method. BaF_2, ZnO, H_3BO_3 and LiF were weighted at a molar ratio of 2:2:6:7. The temperature was raised to 1060 ^oC and kept for 10 h to melt the mixture into solution completely. Then the homogenized solution was slowly cooled to 700 ^oC at a rate of 2 $^oC/h$ and finally cooled to room temperature (RT) at a rate of 20 $^oC/h$. The colorless, block crystals were observed on the surface of the platinum crucible.

Polycrystalline Synthesis. The polycrystalline sample of $BaLiZn_3(BO_3)_3$ was obtained by traditional high temperature solid-state reaction. The raw materials of Li_2CO_3, $BaCO_3$, ZnO and H_3BO_3 in stoichiometric ratio were carefully weighed and packed into a corundum crucible after mixed in an agate mortar. The mixture was preheated at 300 ^oC for 10 h. Then the temperature was raised to 700 ^oC with intermediate grindings and mixings per 50 ^oC and kept for 2 weeks. The purity of the sample was confirmed by powder X-ray diffraction (XRD), which was performed on Bruker D2 PHASER diffractometer equipped with Cu Kα radiation at RT. The diffraction patterns were recorded with the 2θ range from 10° to 70°, the scanning step width was 0.02 °and the scanning rate was 1 s/step. The powder X-ray diffraction patterns of polycrystalline sample shows good agreements with the calculated one (Fig. 1(b)).

1.2 Structure Determination

The crystal structures of $BaLiZn_3(BO_3)_3$ was determined at RT by single-crystal X-ray diffraction on an APEX II CCD diffractometer using monochromatic Mo Kα radiation and integrated with the SAINT program.[1] The single crystal data were analyzed with the *Olex*2 program.[2] The structure was solved using Intrinsic Phasing method provide by the *ShelXT* structure solution program and refined using the *ShelXL* least-squares refinement package.[3] The program PLATON was used for verifying possible missing symmetry elements,[4] but no higher symmetries were found. Crystal data and details of the crystal parameters, data collection, and refinement are listed in Table1. The atomic coordinates, equivalent isotropic displacement parameters and selected bond lengths are summarized in Tables S1-S2, respectively. During the structural determination of $BaLiZn_3(BO_3)_3$, the site occupancy of the Li(1) and Zn(2) atoms were constrained as 0.5 to optimize the R indices and U(eq) values.

1.3 Thermal Analysis

Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) of title compound were investigated using a NETZSCH STA 449C simultaneous thermal analyzer. The sample and reference Al_2O_3 were placed in a platinum crucible and heated at a rate of 5 ℃/min from 40 to 1000 ℃, then cooled to 200 ℃ at a rate of 5 ℃/min under flowing of N_2.

1.4 IR Spectroscopy

The samples were mixed thoroughly with dried KBr at a mass ratio of 1:100 for the measurement of the infrared (IR) spectra for title compound. Data were recorded by a Shimadzu Affinity-1 Fourier transform IR spectrometer in the range of 400-4000 cm^{-1} at RT.

1.5 UV-Vis-NIR Diffuse-Reflectance Spectroscopy

UV-Vis-NIR diffuse-reflectance data for the polycrystalline powder of title compound was collected at RT using a Shimadzu Solid Spec-3700DUV Spectrophotometer with the measurement range extended from 190 to 2600 nm. The Kubelka-Munk function was applied to convert the reflectance spectra to absorbance data.[5]

2. Results and Discussion

2.1 IR and UV-Vis-NIR Spectroscopy

IR spectra of the title compound is measured and given in Fig. S3. The absorption peaks can be assigned as follow. The peaks at 1159 and 1203 cm^{-1} are mainly attributed to the asymmetric stretching of $B_{(3)}$-O, while those at 669 and 709 cm^{-1} are assigned to the out-of-plane bending of $B_{(3)}$-O. The IR spectra further confirm the existence of BO_3 triangles in the structures, which are consistent with the results obtained from the crystallographic structures.[6] The diffuse reflectance spectra indicate that the optical band gaps of $BaLiZn_3(BO_3)_3$ is approximately 5.61 eV (Fig. S4). The wide transparency window will be favorable for the application of $BaLiZn_3(BO_3)_3$ in the UV.

References

(1) SAINT, version 7.60A; Bruker Analytical X-ray Instruments, Inc.: Madison, WI, 2008.

(2) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.

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(5) (a) P. Kubelka and F. Z. Munk, *Tech. Phys.*, 1931, **12**, 593; (b) Tauc, *J. Mater. Res. Bull*. 1970, **5**, 721.

(6) (a) E. R. Lippincott, *J. Amer. Chem. Soc.*, 1963, **85**, 3532; (b) U. Moryc and W. S. Ptak, *J. Mol. Struct.*, 1999, **511**, 241.

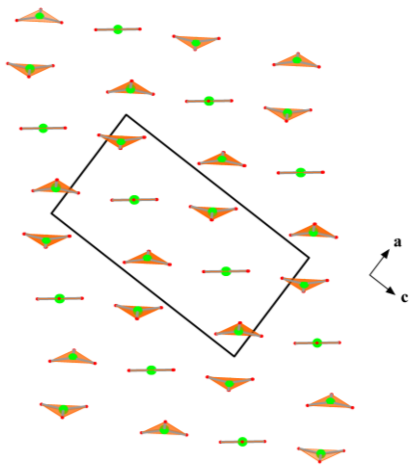
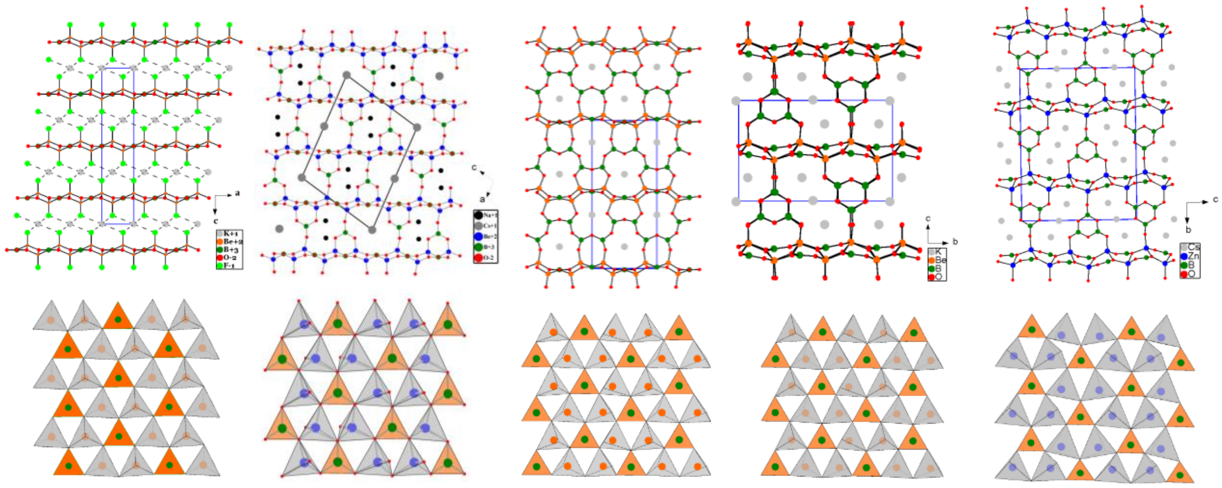


Fig. S1 Nearly coplanar arrangement of BO_3 triangles in $BaLiZn_3(BO_3)_3$.



KBe_2BO_3F (KBBF)	$Na_2Cs_2Be_6B5O15$	β-$KBe_2B_3O_7$	γ-$KBe_2B_3O_7$	$Cs_3Zn_6B_9O_{21}$
(a)	(b)	(c)	(d)	(e)

Fig. S2 KBBF-derivatives possess similar layer structures.

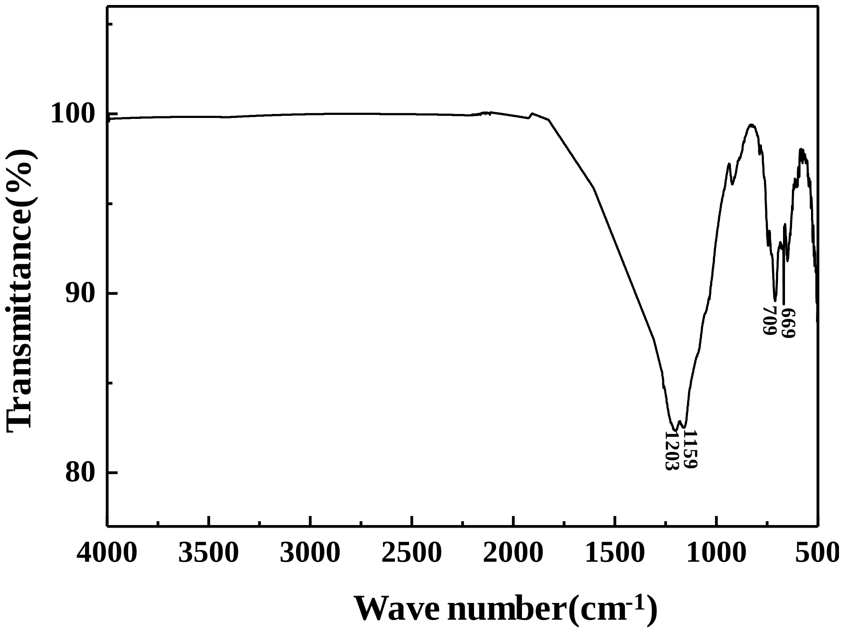


Fig. S3 IR spectrum for $BaLiZn_3(BO_3)_3$.

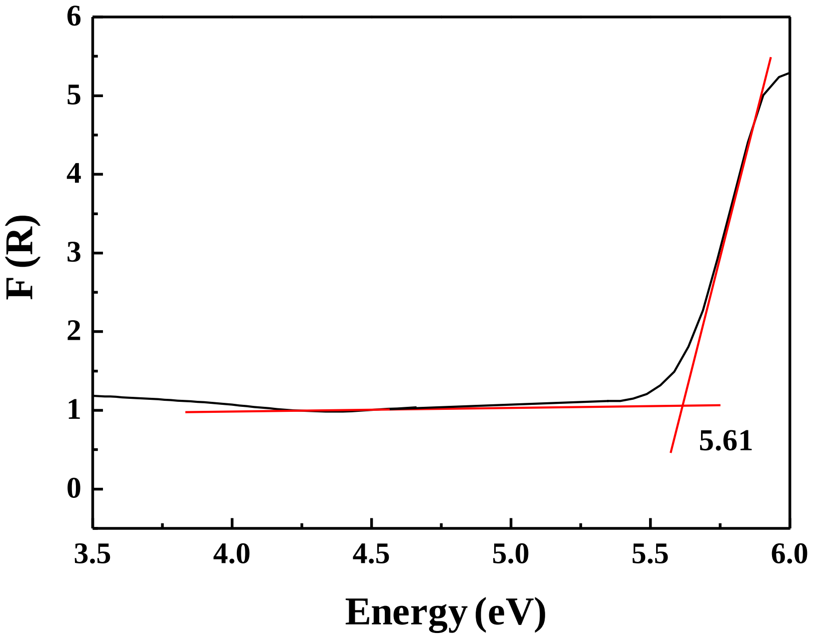


Fig. S4 Absorption spectrum for $BaLiZn_3(BO_3)_3$.

Table S1. Atomic coordinates, equivalent isotropic displacement parameters and and bond valence sum (BVS) for $BaLiZn_3(BO_3)_3$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atoms	S.O.F.	*x*	*y*	*z*	U_{eq}(Å^2)	BVS
Ba(1)	1	0	0.7975(1)	0.2500	0.028(1)	1.566
Zn(1)	1	0.2170(1)	0.3279(1)	0.0614(1)	0.013(1)	2.139
Zn(2)	0.5	0.5085(2)	0.1653(2)	-0.1276(1)	0.014(1)	1.654
Li(1)	0.5	0.5085(2)	0.1653(2)	-0.1276(1)	0.014(1)	
B(1)	1	0.1877(8)	-0.1642(11)	-0.0508(5)	0.008(1)	3.023
B(2)	1	0.5000	0.3264(16)	0.2500	0.013(2)	3.080
O(1)	1	0.2430(5)	0.1027(8)	-0.0676(3)	0.011(1)	2.145
O(2)	1	0.0541(6)	-0.2830(8)	-0.1207(3)	0.015(1)	1.888
O(3)	1	0.3886(6)	0.1821(8)	0.1755(3)	0.018(1)	2.021
O(4)	1	0.2636(6)	-0.2943(8)	0.0389(3)	0.019(1)	2.067
O(5)	1	0.5000	0.6005(12)	0.2500	0.032(2)	2.039

Table S2. Selected bond lengths (Å) and angles (°) for $BaLiZn_3(BO_3)_3$.

Ba(1)-O(1)#1	2.783(4)	Li(1)/Zn(2)-O(5)#8	1.901(4)
Ba(1)-O(1)#2	2.783(4)	Li(1)/Zn(2)-O(1)	1.935(4)
Ba(1)-O(2)#3	3.015(4)	Li(1)/Zn(2)-O(3)#7	1.939(4)
Ba(1)-O(2)#2	2.897(4)	Li(1)/Zn(2)-O(4)#7	1.949(4)
Ba(1)-O(2)#1	2.897(4)	B(1) -O(1)	1.385(7)
Ba(1)-O(2)#4	3.015(4)	B(1) -O(2)	1.354(7)
Ba(1)-O(3) #5	3.327(4)	B(1) -O(4)	1.366(7)
Ba(1)-O(3)#6	3.327(5)	B(2) -O(3) #12	1.366(6)
Ba(1)-O(4)#6	3.187(5)	B(2) -O(3)#10	1.366(6)
Ba(1)-O(4)#5	3.187(5)	B(2) -O(5)	1.352(10)
Ba(1)-O(5) #11	3.432(3)	O(2)-B(1)-O(4)	122.6(5)
Ba(1)-O(5) #12	3.432(3)	O(2)-B(1)-O(1)	119.0(5)
Zn(1)-O(4) #6	1.910(4)	O(4)-B(1)-O(1)	118.3(5)
Zn(1)-O(3)	1.930(4)	O(5)-B(2)-O(3) #12	121.4(3)
Zn(1)-O(1)	1.951(4)	O(5)-B(2)-O(3) #10	121.4(3)
Zn(1)-O(2)#4	1.953(4)	O(3)-B(2)-O(3) #10	117.2(7)

Symmetry transformations used to generate equivalent atoms: #1 x,-y+1,z+1/2 #2 -x,-y+1,-z #3 x,-y,z+1/2 #4 -x,-y,-z #5 -x,y+1,-z+1/2 #6 x,y+1,z #7 -x+1,-y,-z #8 -x+1,-y+1,-z #9 x,y-1,z #10 -x+1,y,-z+1/2 #11 -1+ x,y,z #12 x,y,z

Table S3. Comparison of the interlayer forces |*F*|, interlayer distances and densities of BO_3 in KBBF-type compounds.

compounds	|*F*| (in multiples of |F_{KBBF}|)	Interlayer distance (Å)	BO_3 density ($\times 10^{-3}$)
KBBF	1	6.25	9.43
$BaAlBO_3F_2$	1.82	4.70	10.28
$BaAl_2B_2O_7$	2.87	3.43	11.36
$BaZnBO_3F$	3.31	4.28	10.51
$BaMgBO_3F$	3.40	4.03	11.07
$K_3Ba_3Li_2Al_4B_6O_{20}F$	3.87	3.5	11
$K_3Sr_3Li_2Al_4B_6O_{20}F$	4.52	3.25	10.44
$Sr_2Be_2B_2O_7$	4.94	3.917	13.76
$NaCaBe_2B_2O_6F$	5.26	3.14	15.23
$BaLiZn(BO_3)_3$	6.73	2.92	14.97
$Rb_3Al_3B_3O_{10}F$	7.44	4.37	10.51
$K_2Al_2B_2O_7$	15.52	4.35	11.16
$Na_2CsBe_6B_5O_{15}$	22.58	6.27	9.21
$RbBe_2B_3O_7$	26.06	8.68	6.68
$Cs_3Zn_6B_9O_{21}$	26.10	9.61	5.09
γ-$KBe_2B_3O_7$	26.14	8.69	6.96
β-$KBe_2B_3O_7$	26.22	8.54	6.85