Electronic Supplementary Information

BaZn₃(BO₃)₂F₂: A New Beryllium-free Zincoborate with KBBF-type Structure

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Experimental Section

Crystal Growth. Single crystals of $BaZn_3(BO_3)_2F_2$ were obtained by high-temperature spontaneous crystallization in the air. All raw materials were purchased through commercial channels. BaF_2 , $BaCO_3$, ZnF_2 , $Zn(BF_4)_2$ and H_3BO_3 were weighed at molar ratio: 2:3:10:1:20 and ground in a mortar, and poured into a platinum crucible for heating. The mixture was slowly heated to 1073 K in 20 hours and held for 10 hours. Then, the mixture was cooled to 973 K during 16 hours, cooled to 773 K during 130 hours, cooled to 573 K during 65 hours, cooled to room temperature during 10 hours. Some single crystals were obtained in crucible.

Compounds Synthesis. Polycrystalline powders of $BaZn_3(BO_3)_2F_2$ were synthesized via solid-state reaction using two-stage chemical synthesis method. The mixtures of ZnO and B_2O_3 at molar rate of 3:1 for $Zn_3B_2O_6$ were weighted and heated at 750 °C for three days; subsequently, $Zn_3B_2O_6$ and BaF_2 were mixed at molar rate of 1:1 and heated at 750 °C for 10 hours. With this, the polycrystalline samples of $BaZn_3(BO_3)_2F_2$ were obtained. Although the sample has been calcined many times, there are still some extra peaks which are from the raw and intermediate materials of BaF_2 , $Zn_3B_2O_6$ and ZnO.

Single Crystal Structure Data Collection. The single crystal diffraction data were collected on a Bruker D8 Venture Single Crystal X-ray Diffractometer (Mo K α radiation with $\lambda = 0.71073$ Å) at 300 K. Data integration, cell refinement and absorption corrections of the data were completed by utilizing SAINT program.¹ The structure was solved by direct methods and refined on F² by full-matrix least-squares techniques using the program suite SHELXL.² No missed symmetry was proved using PLATON program.³

Powder X-ray Diffraction Powder x-ray diffraction measurements for the targeted BaZn₃(BO₃)₂F₂ were carried out on a Bruker D2 PHASER diffractometer equipped with Cu K α radiation at room temperature. The 2 θ range is 10-70 ° with a step size of 0.02 ° and a fixed counting time of 1 s/step.

Thermal and Optical Performance Characterization. TG and DSC analyses were

carried out on a simultaneous NETZSCH STA 449 F3 thermal analyzer instrument in a flowing N₂ atmosphere. The powder sample of BaZn₃(BO₃)₂F₂ was placed in the Pt crucible, heated from 40 to 1000 °C at a rate of 5 °C min⁻¹. The infrared spectroscopy was measured on a Shimadzu IR Affinity-1 Fourier transform infrared spectrometer in the 400-4000⁻¹ range. The UV-vis-NIR diffuse-reflectance spectroscopy data were recorded at 25 °C using a powder sample of BaZn₃(BO₃)₂F₂ on a Shimadzu SolidSpec-3700DUV spectrophotometer.

Computational Methods. The first-principles calculations were performed by the plane-wave pseudopotential method implemented in the CASTEP package.⁴ To achieve energy convergence, the kinetic energy cutoff of 850 eV for $BaZn_3(BO_3)_2F_2$ within normal-conserving pseudopotential (NCP) was adopted.⁵ The Monkhorst-Pack k-point meshes in the Brillouin zone was set as $6 \times 6 \times 4$ for $BaZn_3(BO_3)_2F_2$.



Figure S1. The experimental and calculated PXRD patterns of BZBF.

Figure S2. The TG and DSC curves of $BaZn_3(BO_3)_2F_2$.



Figure S3. The IR spectrum of $BaZn_3(BO_3)_2F_2$.



Empirical formula	$BaZn_3(BO_3)_2F_2$
Formula weight	489.07
Temperature/K	300.0
Crystal system	trigonal
Space group	р3
a/Å	4.8900(5)
b/Å	4.8900(5)
$c/{ m \AA}$	7.7146(10)
$\alpha /^{\circ}$	90
β/°	90
$\gamma^{/\circ}$	120
Volume/Å ³	159.76(4)
Ζ	1
$\rho_{calc}g/cm^3$	5.083
μ/mm^{-1}	17.239
<i>F</i> (000)	222.0
Radiation	MoKα ($\lambda = 0.71073$)
2^{θ} range for data collection/°	5.28 to 54.856
Index ranges	$-6 \le h \le 6, -6 \le k \le 6, -10 \le l \le 10$
Reflections collected	4094
Independent reflections	250 $[R_{int} = 0.0471, R_{sigma} = 0.0156]$
Data/restraints/parameters	250/0/24
Goodness-of-fit on F^2	1.218
Final <i>R</i> indexes $[I \ge 2\sigma(I)]^{[a]}$	$R_1 = 0.0098, wR_2 = 0.0245$
Final <i>R</i> indexes (all data) ^[a]	$R_1 = 0.0102, wR_2 = 0.0245$
Largest diff. peak/hole (e/Å ³)	0.43/-0.29

Table S1. Crystal data and structure refinement parameters of $BaZn_3(BO_3)_2F_2$.

 ${}^{a}R_{1} = \sum ||F_{o}| - |Fc|| / \sum |F_{o}|$ and $wR_{2} = [\sum w(F_{o}^{2} - F_{c}^{2})^{2}/wF_{o}^{4}]^{1/2}$ for $F_{o}^{2} > 2\sigma(F_{o}^{2})$.

Atom	x	у	z	U _{eq} (Å ²)	BVS
Ba1	0	0	0	10.74(13)	1.844
Zn1	0	0	0.5	7.68(15)	1.981
Zn2	0.666667	0.333333	0.71259(6)	8.63(13)	2.000
B1	0.333333	0.666667	0.6735(5)	8.5(7)	2.976
01	0.2957(3)	0.3687(3)	0.67063(17)	10.8(3)	1.992
F1	0.666667	0.333333	0.9679(3)	15.2(4)	0.912

Table S2. Atomic coordinates equivalent isotropic displacement parameters and bondvalence sum (BVS) for $BaZn_3(BO_3)_2F_2$.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Bal	10.51(13)	10.51(13)	11.20(19	0	0	5.25(7)
)			
Znl	7.44(19)	7.44(19)	8.2(3)	0	0	3.72(9)
Zn2	7.33(15)	7.33(15)	11.3(2)	0	0	3.66(8)
B1	10.2(11)	10.2(11)	5.2(19)	0	0	5.1(5)
01	8.6(6)	8.3(6)	15.1(8)	-1.6(5)	-2.0(5)	4.0(5)
F1	16.6(6)	16.6(6)	12.3(11)	0	0	8.3(3)

Table S3. Anisotropic displacement parameters $(Å^{2} \times 10^{3})$ for BaZn₃(BO₃)₂F₂.

Ba1-O1 ¹	3.0316(14)	Zn1-O1	2.1135(13)
Ba1-O1 ²	3.0316(14)	Zn1-O1 ¹¹	2.1135(13)
Ba1-O1 ³	3.0316(14)	Zn1-O1 ¹²	2.1135(13)
Ba1-O1 ⁴	3.0316(14)	Zn1-O1 ¹³	2.1135(13)
Ba1-O1 ⁵	3.0316(14)	Zn1-O1 ¹⁴	2.1135(13)
Ba1-O1 ⁶	3.0316(14)	Zn2-O1 ³	1.9338(14)
Ba1-F1 ⁷	2.8341(4)	Zn2-O1 ¹⁵	1.9338(14)
Ba1-F1 ⁴	2.8341(4)	Zn2-O1	1.9338(14)
Ba1-F1 ⁸	2.8341(4)	Zn2-F1	1.970(2)
Ba1-F1 ⁵	2.8341(4)	B1-O1 ¹⁶	1.3745(13)
Ba1-F1	2.8341(4)	B1-O1 ¹⁷	1.3745(13)
Ba1-F1 ⁹	2.8341(4)	B1-O1	1.3745(13)
Zn1-O1 ¹⁰	2.1135(13)		

Table S4. Selected bond lengths for $BaZn_3(BO_3)_2F_2$.

Symmetry transformations used to generate equivalent atoms:

#1 1+Y,-X+Y,2-Z	#2 1-Y,+X-Y,+Z	#3 1+Y-X,-X,+Z	#4 1+X,+Y,+Z;
#5 1-X,-Y,2-Z	#6 1-Y+X,+X,2-Z	#7 2-X,-Y,2-Z #8	+X,-1+Y,+Z;
#9 2-X,1-Y,2-Z	#10 1+X,+Y,+Z	#11 -1+X,+Y,-1+Z	#12 +Y,-X+Y,1-Z;
#13 -Y,+X-Y,+Z	#14 -Y+X,+X,1-Z	#15 +Y-X,-X,+Z	#16 -X,-Y,1-Z;
#17+X,1+Y,+Z	#18 1+Y-X,1-X,+Z	#19 1-Y,1+X-Y,+Z	#20 +Y-X,1-X,+Z

References and Notes

- 1. SAINT, Version 7.60A, Bruker Analytical X-ray Instruments, Inc., Madison, WI, 2008.
- 2. Sheldrick, G. M. SHELXTL, version 6.12; Bruker Analytical X-ray Instruments, Inc.: Madison, WI, 2001.
- 3. A. L. Spek, J. Appl. Crystallogr. 2003, 36, 7.
- 4. S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. Probert, K. Refson, M. C. Payne, Z. *Kristallogr. Cryst. Mater.*, 2005, 220, 567.
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