Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

$Ba_4Bi_2(Si_{8-x}B_{4+x}O_{29})$ (x = 0.09): A New Acentric Metal Borosilicate as Promising Nonlinear Optical Material

Ru-Ling Tang,[a,b,c] Chun-Li Hu,[a] Fei-Fei Mao,[a] Jiang-He Feng,[a] Jiang-Gao Mao*[a]

Supplementary Index

EXPERIMENTAL SECTION

Materials and Methods. $BaCO_3$ (Tansoole, 99.0%), Bi_2O_3 (Aladdin, 99.99%), BiF_3 (Tansoole, 99.0%), SiO_2 (Sinopharm Chemical Reagent Co., Ltd., 99.99%), H_3BO_3 (Aladdin, 99.99%) were used without further purification. Energy dispersive X-ray spectroscope (EDS, Oxford INCA) were used to microprobe elemental identification and analyses. Powder X-ray diffraction (PXRD) measurements were performed on a Rigaku MiniFlex 600 diffractometer which is equipped with a Cu Kα radiation (λ = 1.540598 Å) within the range of 2ϑ = 10- 70° with a step size of 0.02° at 293K. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were proceeded on a NETZSCH STA449C unit from 30°C to 1000 °C under nitrogen system. UV-vis and NIR transmittance spectra measurements have been implemented on a PerkinElmer Lamda 950 spectrophotometer within the range of 200-2500 nm at room temperature. The reflectance spectra data was transformed to absorbance as referenced by using the Kubelka-Munk function.[1] The Infra-red (IR) spectra were performed on a VERTEX 70 FTIR spectrophotometer from 4000 to 400 cm^{-1}. Modified method of Kurtz and Perry and 1064 nm radiation was utilized as the basic frequency light to measure the powder SHG effects.[2] BBSBO and KDP crystals were sieved and loaded to certain different particle-size ranges from 150 um to 210 μm.

Syntheses. BBSBO crystals were grown from traditional high temperature solid-state reaction. Well-mixed of BiF_3, $BaCO_3$, H_3BO_3, and SiO_2 at the molar ratio of 1.5:1.5:4.5:2 was put on a clean platinum crucible which was placed at a procedural muffle furnace, slowly heated to 840°C and kept for 10h, and then gradually cooled to 700°C , finally just cooled down naturally. A few bulk crystals

were found at the bottom of the platinum crucible. The polycrystalline sample of BBSBO was synthesized by the standard solid-state reaction method. A stoichiometric mixture of $BaCO_3$, Bi_2O_3, SiO_2, and H_3BO_3 was well ground and then kept at 830°C for 3 days with several intermediate grindings and mixings. The phase purity was confirmed by powder XRD analysis (Figure S1).

Single Crystal Structure Determinations. The BBSBO crystal data has been collected at 293(2) K on a Super Nova (Mo) X-ray Source (λ = 0.71073 Å). We used Program CrysAlisPro for the data reduction, and absorption correction was ran by the multi-scan method.[3] In space group *I* $\bar{4}$*2m,* direct methods was adopted to solved the structure and we used a full-matrix least-squares fitting on F^2 based on SHELX-97 to refine the structure.[4] However, when we try to refine with ideal $Ba_4Bi_2(Si_8B_4O_{29})$, it is found that B atom at the site of 8g showed negative displacement parameters and Si atom at the site of 16j is not fully occupied. Hence we deem that there exists mixture of Si and B atoms in the two sites. After treating with mixing of B and Si, the chemical composition is determined to be $Ba_4Bi_2(Si_{8-x}B_{4+x}O_{29})$ (x = 0.09) (BBSBO) and the resultant refinements were significantly improved. The chemical composition is also in agreement with energy dispersive X-ray spectroscope analyses which showed a molar ratio of Bi, Ba, Si, and B atoms of 0.96: 2.05: 4.13: 2.18. By using *PLATON*, the structure of the title compound was checked for possible symmetry absence and none was discovered.[5-7] Information of Crystallographic data and structure refinement; selected bond lengths and angles; atomic coordinates, equivalent isotropic thermal parameters and bond valence analysis are given in Table S1-4.

Computational Description. Because the optical property calculations are infeasible for a disordered structure, theoretical calculations have been conducted for the ideal "$Ba_4Bi_2(Si_8B_4O_{29})$" structural model. Calculations of electronic structure and density of states (DOS) were taken by carrying out a first-principle plane-wave pseudopotential technique on the

foundation of density functional theory (DFT) within the CASTEP code.[8,9] We have applied norm-conserving pseudopotentials and GGA-PBE exchange-correlation function.[10,11] To determine the number of plane waves, a 750 eV kinetic-energy cutoff was adopted and the Brillouin zone numerical integration was implemented by employing a 2 × 2 × 2 Monkhorst-Pack *k*-point sampling. Orbital electrons of Ba $5s^2 5p^6 6s^2$, Bi $5d^{10} 6s^2 6p^3$, Si $3s^2 3p^2$, B $2s^2 2p^1$ and O $2s^2 2p^4$ were regarded as valence electrons. About 580 empty bands were applied to guarantee the convergence of optical property calculations. NLO properties were calculated on the basis of length-gauge formalism within the independent-particle approximation system.[12] Chen's strategies has been employed, which was stemmed from Rashkeev et al.[13] and later advanced by Chen's group.[14]

2. Figures and Tables.

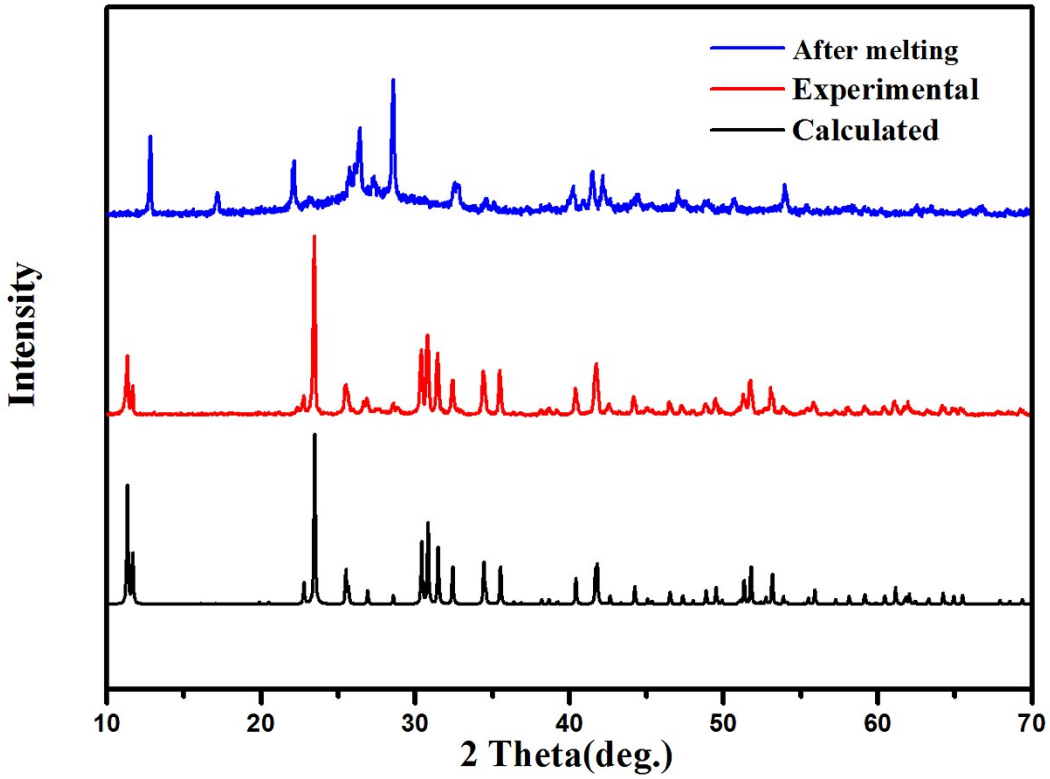

Figure S1 PXRD of BBSBO.

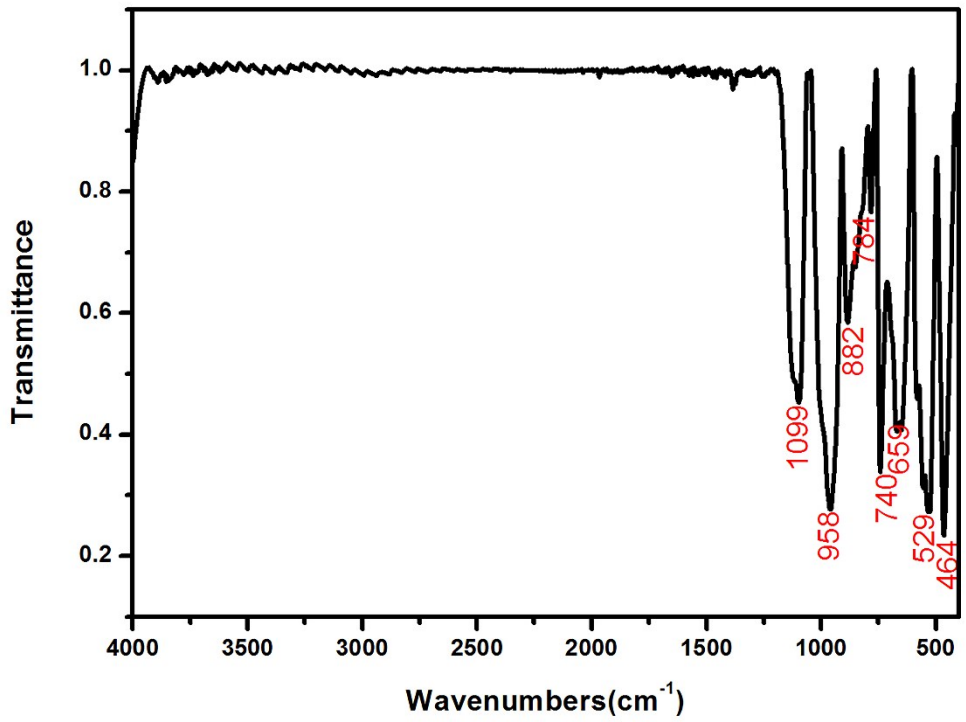

Figure S2 IR spectra of BBSBO.

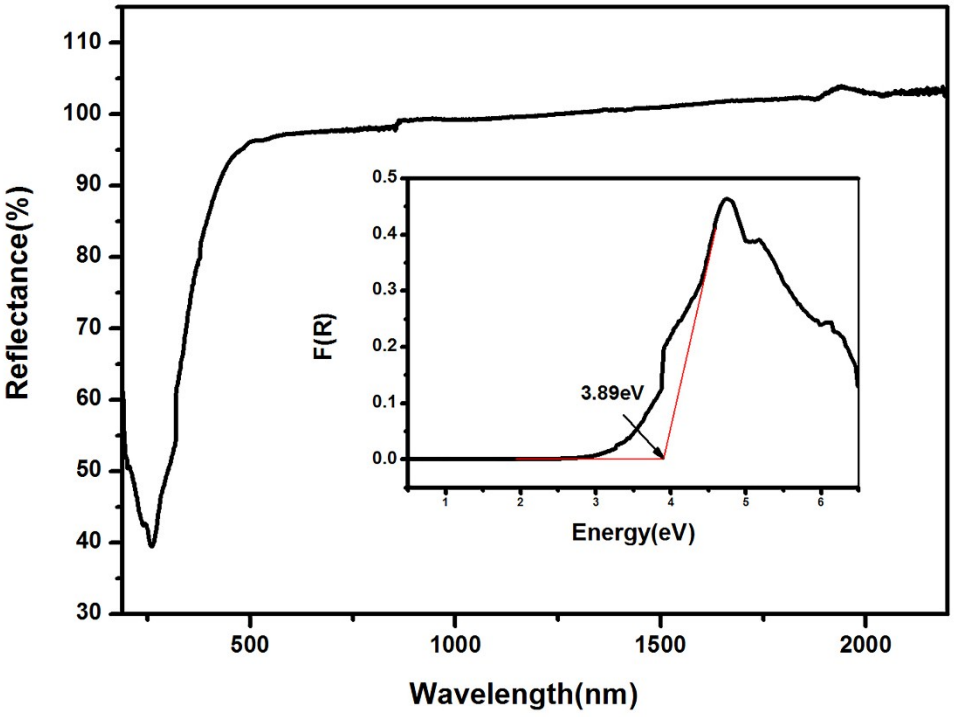

Figure S3 UV-Vis-NIR diffuse reflectance spectra of BBSBO.

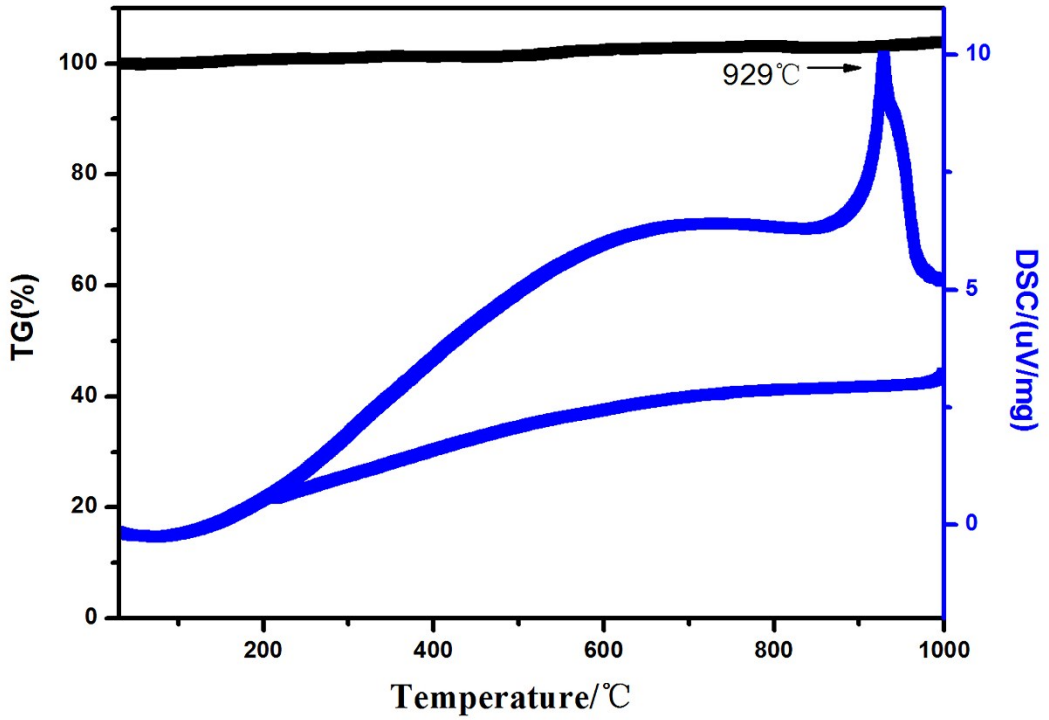

Figure S4 TG and DSC curves of BBSBO.

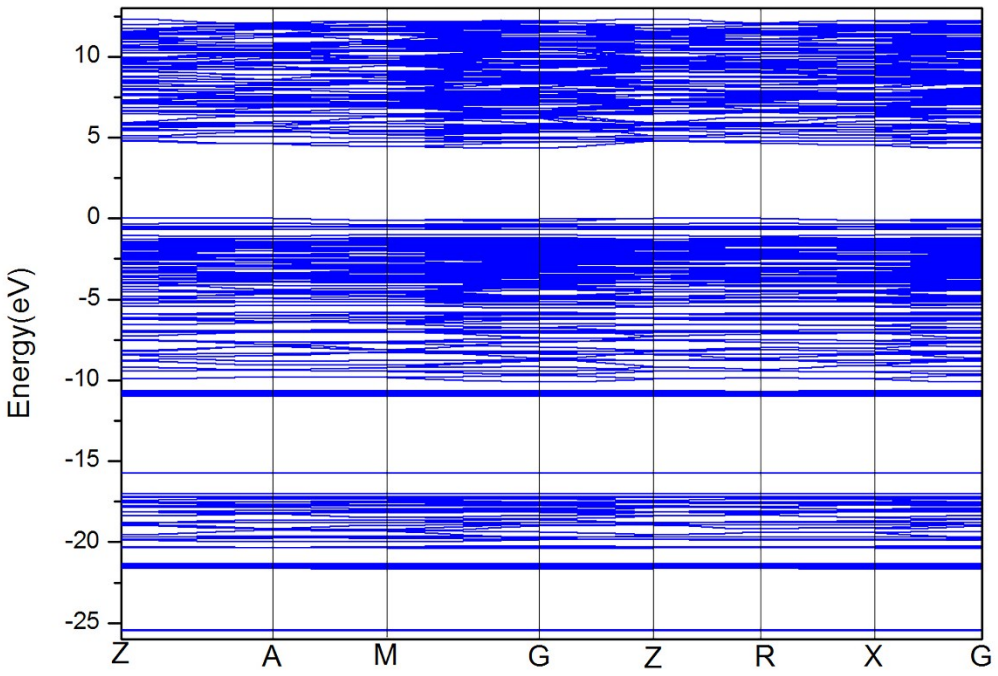

Figure S5. The calculated band structure of BBSBO.

Table S1. Crystal data and structure refinement for BBSBO.

Empirical formula	$Ba_4Bi_2(Si_{7.91}B_{4.09}O_{29})$
Formula weight	1697.72
Temperature	293(2) K
Crystal system	Tetragonal
Space group	$I\bar{4}2m$
a (Å)	11.0254(4)
c (Å)	10.3961(9)
α (°)	90
β (°)	90
γ (°)	90
Volume ($Å^3$)	1263.74
Z	2
Calculated density ($g\ cm^{-3}$)	4.462
Absorption coefficient (mm^{-1})	20.514
F (000)	1506
ϑ range for data collection (°)	3.70 -26.31
Limiting indices	-13<=h<=11, -13<=k<=11, -12<=l<=12
Reflections collected / unique	4257 / 696 [R (int) = 0.0424]
Completeness to ϑ	26.31° 99.0 %
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.032
Final R indices [I>2 σ (I)]	R1 = 0.0168, wR2 = 0.0327
R indices (all data)	R1 = 0.0175, wR2 = 0.0331
Flack factor	0.000(8)
Extinction coefficient	0.00050(5)
Largest diff. peak and hole	0.938 and -0.570 e. $Å^{-3}$

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = \{\sum w[(F_o)^2 - (F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$

Table S2. Selected bond distances (Å) and angles (deg) for BBSBO.

Bi (1)-O (5)	2.0748(3)	B (2)-O (4)	1.490(3)
Bi (1)-O (1) #3	2.327(3)	B (2)-O (4) #11	1.490(3)
Bi (1)-O (1) #7	2.327(3)	B (2)-O (3)	1.510(4)
Bi (1)-O (1) #8	2.327(3)	B (2)-O (3) #12	1.510(4)
Bi (1)-O (1)	2.327(3)	O (3)-Si (1)-O (1)	115.0(2)
Ba (1)-O (1) #1	2.734(5)	O (3)-Si (1)-O (2) #10	109.08(18)
Ba (1)-O (1) #2	2.734(5)	O (1)-Si (1)-O (2) #10	110.0(3)
Ba (1)-O (1)	2.838(5)	O (3)-Si (1)-O (2)	108.0(2)
Ba (1)-O (1) #3	2.838(5)	O (1)-Si (1)-O (2)	104.2(2)
Ba (1)-O (3) #4	2.842(3)	O (2) #10-Si (1)-O (2)	110.4(3)
Ba (1)-O (3) #5	2.842(3)	O (4)-B (2)-O (4) #11	115.1(5)
Ba (1)-O (4) #5	3.119(5)	O (4)-B (2)-O (3)	107.3(2)
Ba (1)-O (2)	3.150(4)	O (4) #11-B (2)-O (3)	109.1(2)
Ba (1)-O (2) #3	3.150(4)	O (4)-B (2)-O (3) #12	109.1(2)
Ba (1)-O (5)	3.2092(4)	O (4) #11-B (2)-O (3) #12	107.3(2)
Si (1)-O (3)	1.584(4)	O (3)-B (2)-O (3) #12	108.9(4)
Si (1)-O (1)	1.590(3)		
Si (1)-O (2) #10	1.605(4)		
Si (1)-O (2)	1.618(4)		

Symmetry transformations used to generate equivalent atoms:

#1 x, -y+2, -z; #2 -y+2, x, -z; #3 y, x, z; #4 -y+3/2, -x+3/2, z-1/2; #5 -x+3/2, -y+3/2, z-1/2; #6 y-1/2, -x+3/2, -z+1/2; #7 -x+2, -y+2, z; #8 -y+2, -x+2, z; #9 y, -x+2, -z; #10 -y+3/2, x+1/2, -z+1/2; #11 y, -x+2, -z+1; #12 x, -y+2, -z+1; #13 -x+3/2, -y+3/2, z+1/2; #14 -y+2, x, -z+1.

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å ^{2} x 10^3) for BBSBO.

Atom	x	y	z	Wyckoff	Occupancy	U(eq)
Ba(1)	7942(1)	7942(1)	-1(1)	8i	1	16(1)
Bi(1)	10000	10000	1996(1)	4e	1	11(1)
Si(1)	6958(1)	9859(2)	2662(1)	16j	0.926	8(1)
B(1)	6958(1)	9859(2)	2662(1)	16j	0.074	8(1)
B(2)	8291(4)	10000	5000	8g	0.875	6(2)
Si(2)	8291(4)	10000	5000	8g	0.125	6(2)
O(1)	7932(3)	10057(5)	1554(3)	16j	1	14(1)
O(2)	6083(3)	8800(4)	2112(3)	16j	1	17(1)
O(3)	7496(3)	9415(3)	3994(3)	16j	1	10(1)
O(4)	9017(3)	9017(3)	5612(4)	8i	1	9(1)
O(5)	10000	10000	0	2a	1	16(2)

Table S4. Calculated bond valence sum (BVS) for BBSBO.

Atom	O(1)	O(2)	O(3)	O(4)	O(5)	BVS
Ba(1)	0.301(×4) +0.227(×2)	0.098(×2)	0.225(×2)	0.106	0.083	1.892
Bi(1)	0.527(×2)	-	-	-	1.042	3.150
Si(1)	1.096	1.056+1.014	1.114	-	-	4.280
B(2)	-	-	0.689(×2)	0.725(×2)	-	2.827

Table S5. The state energies (eV) of the lowest conduction band (LCB) and the highest valence band (HVB) for BBSBO.

Compound	k-point	LCB	HVB
$Ba_4Bi_2(Si_{7.91}B_{4.09}O_{29})$	Z (0.000, 0.000, 0.500)	4.81842	-0.00244
	A (0.500, 0.500, 0.500)	4.60578	-0.00041
	M (0.500, 0.500, 0.000)	4.45306	-0.10484
	G (0.000, 0.000, 0.000)	4.34993	-0.15593
	Z (0.000, 0.000, 0.500)	4.81842	-0.00244
	R (0.000, 0.500, 0.500)	4.68341	0
	X (0.000, 0.500, 0.000)	4.51591	-0.10653
	G (0.000, 0.000, 0.000)	4.34993	-0.15593

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