Supporting Information

$PbBe_2B_2O_6$: An Excellent Ultraviolet Nonlinear-Optical Crystal with Unprecedented π-π Interacting $BeBO_5$ Group

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Section S1.

Experimental Section

Reagents. As raw materials, BeO (99.9%), H_3BO_3 (99.99%), $PbCO_3$ (99.99%), PbO (99.9%), and PbF_2 (99.99%) were all purchased from Aladdin and used as received.

Crystal Growth. ***Caution!*** *Because of the high toxicity of BeO powder upon inhalation, all of the experiments were performed under sufficient ventilation.* Crystals of $PbBe_2B_2O_6$ were prepared via high-temperature solid-state reactions using PbO-PbF_2-B_2O_3 as the flux. Raw materials $PbCO_3$, BeO, and H_3BO_3 in the molar ratio of 3: 1: 6 were ground thoroughly in an agate mortar, pressed into a pellet, placed in a Pt crucible, and heated in a muffle furnace at 550 °C for 12 h. Then, the material was reground thoroughly, pressed into a pellet, and heated at 650 °C for 24 h. Next, the obtained material (2.98 g), PbO (0.456 g, 2 mmol), and PbF_2 (0.981 g, 4 mmol) were ground thoroughly in an agate mortar, pressed into a pellet, and gradually heated at 670 °C for 36 h to ensure homogeneity. The temperature was then lowered to 590 °C at a rate of 2 °C/h, cooled to 500 °C at a rate of 1 °C/h, and finally cooled to 350 °C at a rate of 1.5 °C/h before the furnace was turned off. Colorless and transparent block millimetre-sized crystals were obtained after dissolving the flux in water. The $PbBe_2B_2O_6$ crystals were soaked in distilled water for two months at ambient temperature to evaluate the water stability (Figure S1a). There is little change in the shape or weight loss after drying (Figure S1b), showing that the $PbBe_2B_2O_6$ crystal is water-insoluble at ambient temperature.

Characterization

Single-Crystal X-Ray Diffraction (XRD). Single-crystal XRD data were collected on a Bruker D8 Venture diffractometer at 293 K using graphite-monochromized Mo K_α radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods with the program *SHELXS* and refined by the full-matrix least-squares program *SHELXL*.[1] The structure had been carefully checked by the program *PLATON*[2] and no higher symmetries were found. The details of relevant crystallographic data are summarized in Table S2. The atomic coordinates and equivalent isotropic displacement parameters are listed in Table S3. The selected bond distances and angles are showed in Table S4.

Powder X-Ray Diffraction (XRD). Powder XRD data were collected using a Bruker Model D8 Advance powder diffractometer equipped with Cu K_α radiation ($\lambda = 1.5418$ Å) in the 2θ angular range of 5–120° with a scan step width of 0.01°. The experimental XRD pattern was in good agreement with the calculated one.

Element Analysis. Element analysis of $PbBe_2B_2O_6$ was performed by a Jobin Yvon Ultima2 inductively coupled plasma optical emission spectrometer (ICP-OES) with Sepex Certiprep standards. The samples were dissolved in the perchloric acid at the boiling point for 30 min.

Thermal Behavior. Thermogravimetry (TG) and differential scanning calorimetry (DSC) analysis of $PbBe_2B_2O_6$ were carried out on a NETZSCH STA 449 F5 Jupiter simultaneous analyze under flowing nitrogen. About 15 mg polycrystalline samples were placed in Pt crucibles, and heated from room temperature to 1050 °C at the rate of 10 °C/min under flowing N_2 atmosphere. The thermogravimetry (TG) and differential scanning calorimetry (DSC) curves of $PbBe_2B_2O_6$ (Figure S2) show that

the weight loss in the TG curve was not obviously observed up to 1000 °C, and an endothermic peak at 852 °C in the DSC curve was detected. Powder XRD of the residues (Figure S3) suggests that $PbBe_2B_2O_6$ is an incongruently melting compound and thereby large crystal should be grown by the flux method. Single-crystals of $PbBe_2B_2O_6$ were grown by using the flux of PbO-PbF_2-B_2O_3.

Solid-State Nuclear Magnetic Resonance (NMR) Spectroscopy. ^{9}Be solid-state magic-angle spinning (MAS) NMR spectroscopy was recorded on a Bruker Avance 600 III HD spectrometer at a magnetic field strength of 14.9 T at room temperature. The experiment was operated at a MAS frequency of 10 kHz with a relaxation delay of 1s and tube diameter of 3.2 mm. In order to further check the local coordination of the BeO_3 unit in $PbBe_2B_2O_6$, three BeO_4-containing structures BeO, $BeSO_4{\cdot}4H_2O$ (99.99%, Aladdin) and our reported $Cs_4LiBe_4P_7O_{24}$[3] were used as the reference samples. The chemical shifts were referenced by using the ^{9}Be shift of $BeSO_4{\cdot}4H_2O$ (δ ^{9}Be = 0.00 ppm). Note that the signal intensities of $PbBe_2B_2O_6$, $Cs_4LiBe_4P_7O_{24}$ and BeO become 6.5, 2.5 and 0.3 times of their original intensity, respectively, to more clearly fulfil the comparison of the chemical shifts.

Infrared (IR) Spectroscopy. Fourier transform infrared (FTIR) spectrum of $PbBe_2B_2O_6$ was recorded from KBr pellets in the range 2000–400 cm^{-1} on a Nicolet Model 5DX spectrometer. FTIR spectra of $PbBe_2B_2O_6$ is shown in Figure S4. The fundamental vibration wavenumbers of BO_3 units in the four distinct peaks 1258, 977, 778 and 608 cm^{-1} are in good agreement with the known borates with BO_3 units.[4] The absorption peaks at 1258, 977 and 853 cm^{-1} are assigned to the asymmetric and the

symmetric stretching vibrations of BO_3 units, respectively. The absorption peaks at 778, 698, 608, and 543 cm^{-1} are attributed to the symmetric and asymmetric bending vibrations of BO_3 units, respectively.

Transmission Spectroscopy. Optical transmission spectrum of the $PbBe_2B_2O_6$ single-crystal was collected on a Shimadzu SolidSpec-3700 spectrometer in the 220−3200 nm region. An unpolished crystal with a size of 6.8 × 2.5 × 1.2 mm^3 was used to perform the measurements.

UV–vis–near-IR Diffuse Reflection Spectroscopy. UV–vis–near-IR diffuse reflection spectrum of $PbBe_2B_2O_6$ was collected at 298 K using powder samples with $BaSO_4$ as a standard on a Cary 5000 UV–Vis–Near-IR spectrophotometer in the range 200–1500 nm. Reflectance spectra were converted to absorbance using the Kubelka–Munk function: $F(R) = (1 - R)^2/2R = K/S$, where R is the reflectance, K is the absorption, and S is the scattering.[5] Measurement of the UV−visible−near-IR diffuse reflectance spectrum shows that $PbBe_2B_2O_6$ has a bandgap (E_g) of 4.13 eV, with a broad optical bandgap (Figure S5).

Second-Harmonic Generation (SHG). Powder SHG measurements of $PbBe_2B_2O_6$ were performed by a Kurtz-Perry method[6] at 298 K. The measurement was carried out with a Q-switched Nd: YAG solid-state laser at a wavelength of 1064 nm. The crystals $PbBe_2B_2O_6$ were ground and sieved into a series of distinct size ranges: 20−40 μm, 40−60 μm, 60−80 μm, 80−120 μm, 120−150 μm, 150−200 μm, and 200−300 μm, which were pressed between quartz glass slides and secured with tape in 1-mm-thick aluminum holders containing a hole 8 mm in diameter. Each of them was then placed

into a light-tight box, and the intensity of frequency-doubled output emitted from the samples was collected through a photomultiplier tube. Polycrystalline KH_2PO_4 (KDP) as the reference were ground and sieved into the same particle size ranges. The SHG signal intensity of the $PbBe_2B_2O_6$/KDP ratio was identified based on the same size (150−200 μm).

Birefringence Measurement. The birefringence of $PbBe_2B_2O_6$ was observed on a CNOPTEC cross-polarizing microscope BK-POLR with a LED light filter. The LED light source has the optical wavelength of 590 ± 3 nm. The birefringence was calculated by using the Eq. 1:

$$R = d \times | Ne - No | = d \times \Delta n$$

where R, d, and Δn represent the optical retardation, thickness of the crystal, and birefringence, respectively.

Bond-valence-sum (BVS) calculations. The bond valence sums were calculated using the formula $V_i = \Sigma S_{ij} = \Sigma \exp[(r_0 - r_{ij})/B]$, where S_{ij} is the bond valence associated with the bond length r_{ij}, and r_0 and B (usually 0.37) are empirically determined parameters.[7]

Computational Method

Density functional theory (DFT) calculations.

First-principles calculations were performed by using CASTEP package based on density functional theory (DFT).[8] The functional developed by Perdew, Burke and Ernzerhof (PBE) in the generalized gradient approximation (GGA) form was adopted to describe the exchange-correlation energy.[9] The optimized norm-conserving pseudopotential[10] for Be, B, Pb, and O allowed us to use a small plane-wave basis set

without compromising the accuracy required for the calculation. A kinetic energy cutoff of 800 eV and Monkhorst-Pack[11] k-point mesh spanning less than 0.03 $Å^{-1}$ in the Brillouin zone were chosen.

The calculated band gap of 3.31 eV (Figure S6) by GGA-PBE is smaller than the experimental data (4.13 eV) due to the discontinuity in the exchange-correlation functional, so a scissor operator[12] was used to shift the conduction band upward to agree with the measured data. The imaginary part of the dielectric function of the electronic transition between the valence bands (VB) and the conduction bands (CB) was calculated from the scissor-operator-corrected electronic band structure. The real part of the dielectric function, i.e., the refractive indices, was then determined by a Kramers-Kronig transform. The anisotropic SHG coefficients were calculated using a program developed by our group.[13] To investigate the contribution of the constituent groups to the SHG response, real-space atom-cutting analysis was performed on the crystals.[14] In real-space atom-cutting analysis, when the contribution to the optical properties of a specified ion (or group) is of interest, the wavefunction in the zones belonging to the other ions (groups) is set to zero (which is referred to as "atom cutting"). The contribution of the ion (group) of interest to the n-th polarizability is $\chi^n(X) = \chi^n$ (all the atoms being cut except X). In the SHG-weighted electronic cloud calculations, the probability densities of all occupied (valence) or unoccupied (conduction) states projected onto real space are multiplied by a weighting factor that is related to the contribution to SHG efficiency by the virtual electron (VE) and virtual hole (VH) processes.[15] This ensures that the quantum states irrelevant to SHG are not shown in

the occupied or unoccupied “SHG-densities”, while the orbitals vital to SHG are intuitively highlighted in real space. Single point calculations were carried out at the M06/6-311++G** level[16] based upon structures derived from single-crystal XRD.

To further understand the origin of SHG, the electron densities of the occupied and unoccupied states in the virtual electron (VE) and virtual hole (VH) processes are visualized by the SHG-weighted electron density calculation (Figure S7). In the VE process the O 2p orbitals of BeO_3 and BO_3 units in the occupied states and the anti-π orbitals of BeO_3 and BO_3 units in the unoccupied states have the large SHG contribution. The O 2p orbitals of PbO_4 units in the occupied states and the Pb lone-pair in the unoccupied states manifest the considerable SHG density. In the VH process the SHG densities mainly arise from BeO_3, BO_3 and PbO_4 with active lone-pair. The analyses show that BeO_3, BO_3, and PbO_4 units are responsible for strong SHG response.

Table S1. Reported Pb(II)-containing borates with stereochemically-active lone-pair.

Compounds	Space group	BO_3 existence	BO_4 existence	References
$Pb_4O(BO_3)_2$	*Aba*2	Yes	No	17
$Pb_2O[BO_2(OH)]$	*C*2/*m*	Yes	No	18
$PbCaB_2O_5$	$P\bar{1}$	Yes	No	19
$Ba_2Pb(B_3O_6)_2$	$P\bar{3}c$	Yes	No	20
$PbBiBO_4$	$P2_1/n$	Yes	No	21
$PbBiBO_4$	*Cmca*	Yes	No	21
$Pb_6B_3O_{10}X$ (X = F, Cl, Br)	*Pbcm*	Yes	No	22
Pb_3OBO_3F	*Pbcm*	Yes	No	23
Pb_2BO_3F	$P6_3/m$	Yes	No	24
Pb_2BO_3Cl	*P*321	Yes	No	25
$Pb_4O[Pb_2(BO_3)_3Cl]$	*Pbcm*	Yes	No	26
Pb_2BO_3Br	*P*321	Yes	No	27
$[O_2Pb_3]_2(BO_3)Br$	*Cmcm*	Yes	No	28
$Pb_2(O_4Pb_8)(BO_3)_3Br_3$	*C*2/*c*	Yes	No	29
$Pb_2(O_8Pb_{12})(BO_3)_2Br_6$	*C*2/*c*	Yes	No	29
$Pb_{10}O_4(BO_3)_3I_3$	*Cc*	Yes	No	30
$[O_2Pb_3]_2(BO_3)I$	*Pmmn*	Yes	No	31
$Pb_2Ba_3(BO_3)_3Cl$	$C222_1$	Yes	No	32
$Pb_2Ba_3(BO_3)_3Br$	$C222_1$	Yes	No	33
$Pb_6Ba_2(BO_3)_5X$ (X = Cl, Br)	*C*2/*m*	Yes	No	34
$PbMBO_4$ (M = Cr, Mn, Fe)	*Pnma*	Yes	No	35
$PbAlBO_4$	*Pnma*	Yes	No	36
$PbAlBO_4$	*Pbcn*	Yes	No	37
$PbMn_{0.5}Al_{0.5}BO_4$	*P*4/*mbm*	Yes	No	37
$PbMn_{0.5}Al_{0.5}BO_4$	*Pnam*	Yes	No	38
Pb_4VBO_8	$P2_1/c$	Yes	No	39
$Pb_6B_2WO_{12}$	*Cmcm*	Yes	No	40
$Pb_2CuB_2O_6$	$P2_1/c$	Yes	No	41
$PbZn_2(BO_3)_2$	*Pccn*	Yes	No	42
$(Pb_3O)_2(BO_3)_2WO_4$	*Cmcm*	Yes	No	43
$Pb_{1-x}Sr_xMnBO_4$ (x = 0, 0.5)	*Pnma*	Yes	No	44
$Li_2Pb_2CuB_4O_{10}$	*C*2/c	Yes	No	45
$Pb_2Mg_2TeB_2O_{10}$	*Cmca*	Yes	No	46
α/β/γ-$Pb_2Ba_4Zn_4B_{14}O_{31}$	*P*1, *Cc*, $P3_2$	Yes	No	47
α/β/γ-$Pb_5Zn_4B_6O_{18}$	$P2_1$/c, $P\bar{1}$, $P2_1$/c	Yes	No	48
$Pb_7O(OH)_3(CO_3)_3(BO_3)$	$P6_3mc$	Yes	No	49

$Pb_2(BO_3)(NO_3)$	$P6_3mc$	Yes	No	50
$Pb_4O(BO_3)(PO_4)$	$P2_1/c$	Yes	No	51
$LiPb_4(BO_3)(PO_4)_2$	*Pbca*	Yes	No	52
$Pb_4(BO_3)_2(SO_4)$	$P2_1/c$	Yes	No	53
$Pb_2[(BO_2)(OH)](SO_4)$	$P2_1/m$	Yes	No	53
$Pb_{47}O_{24}(OH)_{13}Cl_{25}(BO_3)_2(CO_3)$	*Cm*	Yes	No	54
$[Pb_{32}O_{18}][Pb_4Mn_2O]Cl_{14}(BO_3)_8 \cdot 2H_2O$	*Pmmn*	Yes	No	55
$[Pb_7(OH)_3F(BO_3)_2(CO_3)][Mg_{4.5}(OH)_3(Si_5O_{14})]$	$P\bar{1}$	Yes	No	56
$Pb_{24}Mg_9(Si_9AlO_{28})(SiO_4)(BO_3)(CO_3)_{10}(OH)_{14}O_4$	$P\bar{1}$	Yes	No	57
$(Pb_4O)Pb_2B_6O_{14}$	$P\bar{1}$	Yes	Yes	58
$Pb_6B_{10}O_{21}$	$P\bar{1}$	Yes	Yes	59
PbB_4O_7	$P2_1nm$	Yes	Yes	60
$Pb_4B_6O_{13}$	*Cc*	Yes	Yes	61
$Pb_6B_4O_{11}(OH)_2$	*Pnma*	Yes	Yes	62
$Pb_6B_{12}O_{21}(OH)_6$	$P3_2$	Yes	Yes	63
$Pb_6B_{11}O_{18}(OH)_9$	$P3_2$	Yes	Yes	64
$Pb_2B_3O_{5.5}(OH)_2$	*Pnn*2	No	Yes	65
$NaPbB_5O_9$	$P2_1/c$	Yes	Yes	66
$PbCd_2B_6O_{12}$	$P2_1/n$	Yes	Yes	67
$Pb_4Zn_2B_{10}O_{21}$	*Pbcn*	Yes	Yes	68
$Pb_2Cu_3B_4O_{11}$	*P*2/*n*	Yes	Yes	69
$PbLnB_7O_{13}$ (Ln=Tb, Eu, Gd, Sm)	$P2_1$	Yes	Yes	70
$Pb_3(B_3O_7)(NO_3)$	*Pnma*	Yes	Yes	65
$Pb_6B_2Si_8O_{25}$	$R\bar{3}c$	No	Yes	71
$Na_3Pb[B(O_3POH)_4]$	$I4_1/a$	No	Yes	72
$Pb_4Co_2[B(OH)_2P_2O_8](PO_4)_2Cl$	$P\bar{3}c$	No	Yes	73
$Pb_6(Li_{0.648}Na_{0.192})[B_{12}O_{24}]I_{0.84} \cdot 0.168H_2O$	$R\bar{3}m$	Yes	Yes	74

Table S2. Crystal data and structure refinement for $PbBe_2B_2O_6$.

Empirical formula	$PbBe_2B_2O_6$
Formula weight	342.83
Temperature	293(2) K
Crystal system	Orthorhombic
Space group	$Pmn2_1$
a/Å	10.737(2)
b/Å	4.7501(11)
c/Å	4.5368(11)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	231.39(9)
Z	2
ρ_{calc} g/cm^3	4.920
μ/mm^{-1}	36.403
F(000)	296
Theta range for data collection	3.795 to 30.442°
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.117
Flack parameter	0.46(3)
Extinction coefficient	0.065(4)
Final *R* indexes [I>2σ (I)][a]	R_1 = 0.0173, wR_2 = 0.0425
Final *R* indexes [all data][a]	R_1 = 0.0173, wR_2 = 0.0425

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

Table S3. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for $PbBe_2B_2O_6$. *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	**Wyck.**	**Site**	***x*/*a***	***y*/*b***	***z*/*c***	***U*(eq)**	**BVS**
Pb(1)	2a	m	0	−0.82387(5)	−0.1439(4)	0.01651(17)	1.87
Be(1)	4b	1	−0.2489(11)	−1.3208(16)	−0.207(2)	0.017(2)	2.03
B(1)	4b	1	−0.1581(9)	−1.1617(15)	−0.5750(18)	0.0155(18)	3.22
O(1)	4b	1	0.1363(5)	−0.9042(11)	−0.635(8)	0.0429(18)	1.89
O(2)	4b	1	−0.1327(6)	−1.2016(12)	−0.2800(13)	0.0180(11)	2.18
O(3)	4b	1	−0.2911(6)	−1.6194(13)	−0.2370(12)	0.0172(10)	1.94

Table S4. Selected bond distances (Å) and angles (deg) for $PbBe_2B_2O_6$.

Be(1)−O(1)#4	1.664(14)	O(2)−Be(1)−O(3)	128.9(8)
Be(1)−O(2)	1.409(13)	O(2)−Be(1)−O(1)#4	116.3(6)
Be(1)−O(3)	1.495(10)	O(3)−Be(1)−O(1)#4	113.8 (7)
B(1)−O(1)	1.275(12)	O(1)−B(1)−O(2)#6	107.6(16)
B(1)−O(2)#6	1.379(10)	O(1)−B(1)−O(3)#7	132.8(17)
B(1)−O(3)#7	1.385(10)	O(2)#6−B(1)−O(3)#7	119.3(6)
Pb(1)−O(2)	2.373(6)	O(2)−Pb(1)−O(2)#1	73.8(3)
Pb(1)−O(2)#1	2.373(6)	O(2)−Pb(1)−O(1)#2	90.2(3)
Pb(1)−O(1)#2	2.69(3)	O(2)−Pb(1)−O(1)#3	49.5(3)
Pb(1)−O(1)#3	2.69(3)	O(2)#1−Pb(1)−O(1)#3	49.5(3)
O(2)#1−Pb(1)−O(1)#2	90.2(3)	O(1)#2−Pb(1)−O(1)#3	65.9(8)

Symmetry transformations used to generate equivalent atoms:

#1 −x, y, z; #2 −x, y, z−1; #3 x, y, z−1; #4 x−1/2, −y−2, z−1/2; #5 −x−1/2, −y−3, z+1/2; #6 −x, y, z+1; #7 x+1/2, −y−3, z+1/2

Table S5. Optical properties of reported UV NLO BeO_4-containing beryllium borates and $PbBe_2B_2O_6$.

Compounds	Space group	SHG response	Birefringence	UV cutoff edge (nm)	Ref.
$KBe_2BO_3F_2$	*R*32	1.2 × KDP	Exp. 0.077 @1064 nm	Exp. 147	75
$NaBe_2BO_3F_2$	*C*2	1.4 × KDP	Cal. 0.091 @ 200 nm	Exp. 155	76
$RbBe_2BO_3F_2$	*R*32	1.15 × KDP	Exp. 0.073 @1064 nm	Exp. 160	77
$CsBe_2BO_3F_2$	*R*32	1.28 × KDP	Exp. 0.058 @ 1064 nm	Exp. 151	77
$TlBe_2BO_3F_2$	*R*32	1.0 × KDP	Not reported	Exp. < 200	78
$NH_4Be_2BO_3F_2$	*R*32	1.2 × KDP	Exp. 0.072 @ 1064 nm	Exp. 153	79
α-Be_2BO_3F	*C*2	0.3 × KDP	Not reported	Exp. < 186	80
γ-Be_2BO_3F	*R*32	2.3 × KDP	Cal. 0.099 @ 1064 nm	Cal. 144.8	79
$NaBeB_3O_6$	$Pna2_1$	1.60 × KDP	Cal. 0.080 @ 400 nm	Exp. < 200	81
$Na_2Be_4B_4O_{11}$	*P*1	1.3 × KDP	Cal. 0.047 @ 400 nm	Exp. 171	82
β-$KBe_2B_3O_7$	$Pmn2_1$	0.75 × KDP	Cal. 0.038 @ 400 nm	Cal. 187	82
γ-$KBe_2B_3O_7$	$P2_1$	0.68 × KDP	Cal. 0.059 @400 nm	Cal. 186	82
$RbBe_2B_3O_7$	$Pmn2_1$	0.79 × KDP	Cal. 0.038 @ 400 nm	Cal. 179	82
$LiNa_5Be_{12}B_{12}O_{33}$	*Pc*	1.4 × KDP	Cal. 0.046 @ 400 nm	Exp. 169	82
$Na_2CsBe_6B_5O_{15}$	*C*2	1.17 × KDP	Cal. 0.015 @ 400 nm	Cal. 192	83
$Sr_2Be_2B_2O_7$ (SBBO)	$P\bar{6}c2$	3.8 × KDP	Exp. 0.062 @ 1064 nm	Exp. 155	84
$Ba_2Be_2B_2O_7$	$P\bar{6}c2$	2.0 × KDP	Not reported	Exp. 175	85
$BaBe_2BO_3F_3$	$P6_3$	0.3 × KDP	Cal. 0.051 @ 800 nm	Exp. < 185	86
$Sr_3Be_{1.9}B_{5.1}O_{12.1}F_{0.9}$	*R*3*m*	2.2 × KDP	Cal. 0.051 @ 800 nm	Exp. < 200	87
$LiSr_3Be_3B_3O_9F_4$	*R*3*m*	2.2 × KDP	Cal. 0.045 @ 1064 nm	Exp. 175	88
$NaSr_3Be_3B_3O_9F_4$	*R*3*m*	3.0 × KDP	Exp. 0.056 @ 1064 nm	Exp. 170	89

$NaCaBe_2B_2O_6F$	*Cc*	0.3 × KDP	Cal. 0.058 @ 400 nm	Exp. 185	90
$YBe_2B_5O_{11}$	$Pna2_1$	0.9 × KDP	Not reported	Exp. < 200	91
$GdBe_2B_5O_{11}$	$Pna2_1$	1.1 × KDP	Not reported	Exp. < 200	92
$LaBeB_3O_7$	$Pmn2_1$	1.1 × KDP	Not reported	Exp. 220	93
$Sr_2Pb(BeB_5O_{10})(BO_3)$	*R*3*m*	8.0 × KDP	Cal. 0.10 @ 1064 nm	Exp. 280	94
$PbBe_2B_2O_6$	**$Pmn2_1$**	**18.5 × KDP**	**Exp. 0.171 @ 590 nm**	**Exp. 249**	**This work**

Table S6. Optical properties of the main UV NLO borates, carbonates and nitrates.

Compounds	Space group	SHG response	Birefringence	Exp. UV cutoff edge (nm)	Ref.
LiB_3O_5	*Pnc*2	2.6 × KDP	Exp. 0.045@1064 nm	160	95
CsB_3O_5	$P2_12_12_1$	2.0 × KDP	Exp. 0.059@1064 nm	170	96
$CsLiB_6O_{10}$	$I\bar{4}2d$	3.0 × KDP	Exp. 0.049@1064 nm	180	97
β-BaB_2O_4	*R3c*	5.5 × KDP	Exp. 0.113@1064 nm	189	98
BiB_3O_6	*C2*	8.2 × KDP	Exp.0.16@1064nm	286	99
$Li_4Sr(BO_3)_2$	*Cc*	2.0 × KDP	Cal. 0.056@532 nm	186	100
$KSr_4(BO_3)_3$	*Ama*2	1.0 × KDP	Cal. 0.029@1064 nm	300	101
$LiNaB_4O_7$	*Fdd*2	0.2× KDP	Not reported	180	102
$Li_4Rb_3B_7O_{14}$	$P3_121$	0.7× KDP	Not reported	< 190	103
$Li_4Cs_3B_7O_{14}$	$P3_121$	0.5× KDP	Not reported	< 190	104
$Li_6Rb_5B_{11}O_{22}$	*C*2	0.7× KDP	Not reported	< 190	105
$Li_3Cs_2B_5O_{10}$	$C222_1$	0.5× KDP	Not reported	175	106
$Li_5Cs_2B_7O_{14}$	*Ama*2	0.2× KDP	Not reported	< 200	107
$NaCa_4(BO_3)_3$	*Ama*2	0.5 × KDP	Not reported	300	108
$KCa_4(BO_3)_3$	*Ama*2	0.3 × KDP	Not reported	300	108

$K_{0.59}Rb_{0.41}Ca_4B_3O_9$	*Ama*2	0.4 × KDP	Cal.0.036@1064 nm	＜200	109
$KMgBO_3$	$P2_13$	0.3 × KDP	Not reported	185	110
Al_5BO_9	$Cmc2_1$	0.2 × KDP	Cal. 0.02@1064 nm	202	111
$K_2Al_2B_2O_7$	*P*321	1.0 × KDP	Exp. 0.074@589 nm	180	112
β-$Rb_2Al_2B_2O_7$	*P*321	2.0 × KDP	Not reported	< 200	113
$Cs_2Al_2(B_3O_6)_2O$	$P6_3$	0.5 × KDP	Cal. 0.136@177.3 nm	< 185	114
$Cs_2AlB_5O_{10}$	$P3_12_1$	0.8 × KDP	Cal 0.035@1064 nm	＜190	115
$K_{0.67}Rb_{1.33}Al_2B_2O_7$	*P*321	0.9 × KDP	Cal. 0.054@177.3 nm	188	116
$YAl_3(BO_3)_4$	*R*32	4.4 × KDP	Exp. 0.07@ 1064 nm	170	117
$K_2Ba_4Ga_4Li_2B_6O_{21}$	$P\bar{6}2c$	0.5 × KDP	Not reported	226	118
$BiAlGa_2(BO_3)_4$	*R*32	4.0 × KDP	Not reported	271	119
$YCa_4O(BO_3)_3$	*Cm*	3.0 × KDP	Exp. 0.043@ 589 nm	200	120
$Na_3Gd_2(BO_3)_3$	*Amm*2	1.3 × KDP	Exp. 0.02@1064 nm	207	121
$Na_3La_9O_3(BO_3)_8$	$P\bar{6}2m$	6.0 × KDP	Exp. 0.085@ 1064 nm	270	122
$K_3ScB_6O_{12}$	*R*32	1.3×KDP	Not Report	274	123
$La_2SrB_{10}O_{19}$	*C*2	2.0 × KDP	Cal. 0.031@1064 nm	＜250	124
$Rb_3YB_6O_{12}$	*R*32	0.8 × KDP	Not reported	<200	125
$BaYOBO_3$	$P\bar{6}2m$	2.6×KDP	Not Report	190	126
$K_5Mg_2La_3(BO_3)_6$	$P3_1m$	3.1×KDP	Not Report	<200	127
$Rb_7SrY_2(B_5O_{10})_3$	*R*32	0.9 × KDP	Cal. 0.003@1064 nm	＜300	128
$Y_{0.57}La_{0.72}Sc_{2.71}(BO_3)_4$	*R*32	3.6 × KDP	Not reported	< 200	129
$Rb_7SrGd_2(B_5O_{10})_3$	*R*32	0.5 × KDP	Not reported	<225	130
$K_6NaSrSc_2B_{15}O_{30}$	*R*32	0.7×KDP	Cal. 0.02@1064 nm	248	131
$Cs_3Zn_6B_9O_{21}$	$Cmc2_1$	3.3 × KDP	Cal. 0.062@532 nm	< 200	132

$Ba_2Zn(BO_3)_2$	$Pca2_1$	4.5 × KDP	Not reported	230	133
$Ba_5Zn_4(BO_3)_6$	Pc	2.6 × KDP	Not reported	223	134
$(NH_4)_2B_4SO_{10}$	$C2$	1.1×KDP	Cal. 0.053@1064 nm	252	135
$RbZn_2(BO_3)Si_2O_5$	$Cmc2_1$	0.4×KDP	Cal. 0.021@1064 nm	<190	136
$CsZn_2(BO_3)Si_2O_5$	$Cmc2_1$	0.8×KDP	Cal. 0.022@1064 nm	<190	136
$K_3B_6O_{10}NO_3$	$P3_121$	0.8×KDP	Cal. 0.046@1064 nm	216	137
$K_7CaBi_2B_{15}O_{30}$	$R32$	0.6 × KDP	Not reported	282	138
β-Zn_3BPO_7	$P\bar{6}$	1.5 × KDP	Exp. 0.03@1064 nm	250	139
Cd_3BPO_7	$Pna2_1$	2.2 × KDP	Not reported	281	140
$Ba_3(ZnB_5O_{10})PO_4$	$Pmn2_1$	4.0 × KDP	Cal. 0.035@532 nm	180	141
$LiPbB_9O_{15}$	$R3c$	1.0 × KDP	Not reported	261	142
$Pb_4O(BO_3)_2$	$Aba2$	3.0× KDP	Cal. 0.045@532 nm	280	143
$Pb_4B_6O_{13}$	Cc	3.0× KDP	Not reported	290	144
$Be_2(BO_3)(IO_3)$	$Pmc2_1$	7.2×KDP	Cal. 0.172@1064 nm	245	145
$Zn_2BO_3(OH)$	$P2_1$	1.5 ×KDP	Exp. 0.067@800 nm	204	146
$Li(H_2O)_4B(OH)_4·2H_2O$	$P3$	0.8 × KDP	Not reported	262	147
$Na[B_5O_7(OH)_2](H_2O)$	$Pca2_1$	0.1 × KDP	Not reported	221	148
$Na_2B_5O_8(OH)·2H_2O$	$Pna2_1$	0.5 × KDP	Not reported	< 190	149
$Na_2B_9O_{15}(H_2O)(H_3O)$	$P2_1$	1.0 × KDP	Not reported	286	150
$K_3B_3O_4(OH)_4·2H_2O$	$Cmc2_1$	0.8 × KDP	Not reported	< 190	151
$K_2B_5O_8(OH)·2H_2O$	$Pna2_1$	0.8 × KDP	Cal.0.024@1064 nm	＜200	152
$K_2[B_4O_5(OH)_4]·2H_2O$	$P2_12_12_1$	0.5 × KDP	Cal. 0.016@1064 nm	180	153
$Mg[B_6O_9(OH)_2]·4H_2O$	$Pna2_1$	1.1 × KDP	Not reported	< 200	154
$Ca_2B_{11}O_{16}(OH)_5·H_2O$	$P2_1$	1.3 × KDP	Not reported	223	155

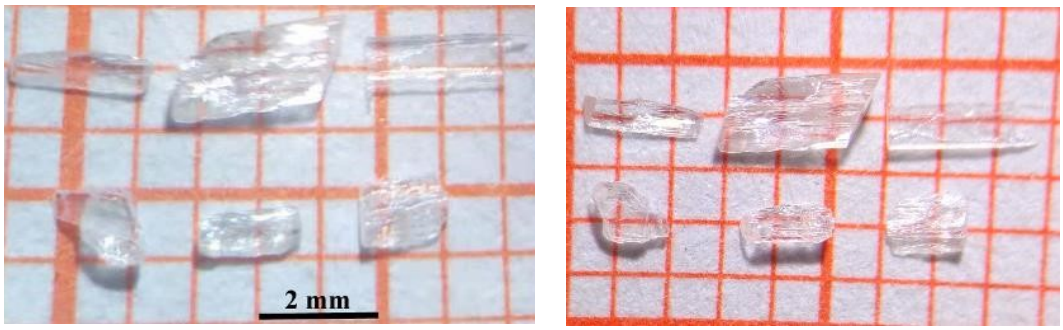
$Ca_2B_5O_9(OH)\cdot H_2O$	*Cc*	3.0 × KDP	Not reported	228	156
$Sr_2B_5O_9(OH)\cdot H_2O$	*C*2	3.0 × KDP	Not reported	< 190	157
$Sr_4B_{10}O_{18}(OH)_2\cdot 2H_2O$	*P*1	2.0 × KDP	Not reported	< 190	158
$Ba_2[B_6O_9(OH)_4]$	$P2_1$	3.0 × KDP	Not reported	< 190	159
$Ba_2[B_4O_7(OH)_2]$	$P3_121$	2.2 × KDP	Not reported	242	160
$Ba_2B_9O_{12}(OH)_7\cdot 4H_2O$	$Pmn2_1$	0.8× KDP	Not reported	230	161
Ba_3 $(B_{10}O_{16})$ $(OH)_4$	*P*31*c*	1.1× KDP	Not reported	243	162
$Ba_2B_{11}O_{16}(OH)_5\cdot H_2O$	$P2_1$	1.2 × KDP	Not reported	<200	163
$Ba_3Al_2B_{10}O_{19}(OH)_4$	*Fdd*2	3.0× KDP	Not reported	230	164
$Ba_3Ga_2B_{10}O_{19}(OH)_4$	*Fdd*2	3.0× KDP	Not reported	248	164
$LiK[B_5O_8(OH)]\cdot 1.5H_2O$	$C222_1$	1.3 × KDP	Not reported	＜200	165
$Na_{0.33}K_{1.67}(B_4O_5)(OH)_4\cdot 3H_2O$	$P\bar{6}2c$	0.9 × KDP	Not reported	242	166
$Li_2CsB_7O_{10}(OH)_4$	*C*222	2.5 × KDP	Cal. 0.06@1064 nm	＜190	167
$Li_{0.5}Ca_{0.5}B_{3.5}O_{5.5}$ (OH)	$P3_221$	1.6×KDP	Not Report	213	168
$NaSr_3B_{10}O_{16}$ $(OH)_5$	$P3_1c$	3.3×KDP	Cal. 0.039@1064 nm	＜190	169
$Cs_2CaB_8O_{10}(OH)_8\cdot 8H_2O$	$P2_12_12_1$	0.5 × KDP	Not reported	190	170
$K_2BaB_8O_{10}(OH)_8\cdot 10H_2O$	$Pna2_1$	0.5 × KDP	Not reported	< 200	171
$LiBa_3(OH)(B_{10}O_{16})$ $(OH)_5$	*P*31*c*	1.2 × KDP	Not reported	< 200	172
$NaPb_4B_{11}O_{21}\cdot H_2O$	*Pnn*2	2.0 × KDP	Not reported	< 220	173
$Ba_{2.16}Pb_{0.84}B_{10}O_{16}$ $(OH)_4$	*P*31*c*	1.2 × KDP	Not reported	266	162
$Ba_2B_5O_9Cl\cdot 0.5H_2O$	*Pnn*2	1.0 × KDP	Not reported	225	174
$Zn_2BO_3X\cdot H_2O$ (X = Cl, Br)	$P2_12_12_1$	0.6 × KDP	Not reported	<210	175
$NH_4B_4O_6F$	$Pna2_1$	3.0 × KDP	Exp. 0.117@1064 nm	156	176

$Li_2B_6O_9F_2$	*Cc*	0.9 × KDP	Cal. 0.07@1064 nm	< 190	177
$Ca_5(BO_3)_3F$	*Cm*	2.0× KDP	Exp. 0.05@1064 nm	190	178
RbB_4O_6F	$Pna2_1$	0.8 × KDP	Exp. 0.102@1064 nm	< 190	179
$K_{10}B_{13}O_{15}F_{19}$	*R*3*m*	0.4 × KDP	Cal. 0.03@1064 nm	＜190	180
$Rb_{10}B_{13}O_{15}F_{19}$	*R*3*m*	0.5 × KDP	Cal. 0.026@1064 nm	＜190	180
CsB_4O_6F	$Pna2_1$	1.9 × KDP	Exp. 0.114@1064 nm	155	181
$CsKB_8O_{12}F_2$	*P*321	1.9 × KDP	Cal. 0.105@1064 nm	< 190	179
$CaB_5O_7F_3$	$Cmc2_1$	2.0 × KDP	Exp. 0.072@546 nm	< 180	182
$SrB_5O_7F_3$	$Cmc2_1$	1.6 × KDP	Cal. 0.072@589 nm	< 180	183
$Sr_3B_6O_{11}F_2$	$P2_1$	2.5 × KDP	Not reported	< 190	184
$Ba_3B_6O_{11}F_2$	$P2_1$	3.0 × KDP	Not reported	< 200	185
$Ba_4B_{11}O_{20}F$	$Cmc2_1$	10 × KDP	Cal.0.0146@1064 nm	175	186
$PbB_5O_7F_3$	$Cmc2_1$	6.0 × KDP	Cal. 0.12@1064 nm	225	187
$Li_3Ca_9(BO_3)_7{\cdot}2[LiF]$	*P*1	1.0 × KDP	Cal. 0.07@532nm	230	188
β-$BaCaBO_3F$	$P\bar{6}2m$	0.7 × KDP	Exp. 0.047@1064 nm	210	189
$BaMgBO_3F$	*Cc*	0.1 × KDP	Cal. 0.058@1064 nm	190	190
$Ba_3Sr_4(BO_3)_3F_5$	$P6_3mc$	0.5 × KDP	Not reported	210	191
$Rb_3Al_3B_3O_{10}F$	$P3_1c$	1.2 × KDP	Not reported	<200	192
$BaAlBO_3F_2$	$P\bar{6}2c$	2.0 × KDP	Not reported	165	193
$BaAl_{0.61}Ga_{0.39}BO_3F_2$	$P\bar{6}2c$	2.0 × KDP	Not reported	265	194
$CsAlB_3O_6F$	$Pna2_1$	2.0 × KDP	Cal. 0.091@532 nm	< 190	195
$RbAlB_3O_6F$	$Pna2_1$	0.2×KDP	Cal 0.095@1064 nm	<200	196
$Cs_{0.5}Rb_{0.5}AlB_3O_6F$	$P\bar{6}2c$	2×KDP	Not Report	<200	196

$K_3Ba_3Li_2Al_4B_6O_{20}F$	$P\bar{6}2c$	1.5 × KDP	Cal. 0.052@532 nm	190	197
$Rb_3Ba_3Li_2Al_4B_6O_{20}F$	$P\bar{6}2c$	1.4 × KDP	Cal. 0.057@1064nm	195	198
$K_3Sr_3Li_2Al_4B_6O_{20}F$	$R32$	1.7 × KDP	Exp.0.0574@1064 nm	190	199
$CsZn_2BO_3F_2$	$R32$	3.2×KDP	Not Report	<190	200
$CsZn_2BO_3Cl_2$	$R32$	2.8×KDP	Not Report	<190	200
$CsZn_2BO_3FCl$	$R3$	3.5×KDP	Not Report	<190	201
$BaZnBO_3F$	$P\bar{6}$	2.8× KDP	Not reported	223	202
$Cd_5(BO_3)_3F$	Cm	3.8 × KDP	Not reported	282	203
$PbB_2O_3F_2$	$P3_1m$	13 × KDP	Not reported	220	204
$Pb_3B_6O_{11}F_2$	$P2_1$	4.0 × KDP	Cal. 0.071 @ 532 nm	240	205
$K_3B_6O_{10}Cl$	$R3m$	4.0 × KDP	Exp. 0.047@ 800 nm	180	206
$K_3B_6O_{10}Br$	$R3m$	3.0 × KDP	Not reported	184	207
$K_{2.33}Na_{0.67}B_6O_{10}Br$	$R3m$	2.8 × KDP	Not reported	< 190	208
$K_{2.87}Na_{0.13}B_6O_{10}Br$	$R3m$	2.8 × KDP	Not reported	< 190	208
$Ca_2B_5O_9Cl$	$Pnn2$	0.8 × KDP	Exp.0.0184@546 nm	170	209
$Sr_2B_5O_9Cl$	$Pnn2$	0.5 × KDP	Exp.0.0149@546 nm	170	209
$NaBa_4(AlB_4O_9)_2Cl_3$	$P4_2nm$	1.0 × KDP	Exp. 0.017@1064 nm	230	210
$NaBa_4(AlB_4O_9)_2Br_3$	$P4_2nm$	1.0 × KDP	Exp.0.0287@532 nm	248	211
$Zn_3B_7O_{13}Cl$	$R3c$	2.2 × KDP	Cal.0.024@1064 nm	190	212
$NH_4Zn_2BO_3Cl_2$	$R32$	2.8 × KDP	Not reported	186	213
$KZn_2BO_3Cl_2$	$R32$	3.0 × KDP	Not reported	193	212
$RbZn_2BO_3Cl_2$	$R32$	2.9 × KDP	Not reported	198	213
$KZn_2BO_3Br_2$	$R32$	2.7 × KDP	Not reported	206	213

$RbZn_2BO_3Br_2$	*R*32	2.5 × KDP	Not reported	214	213
$Ba_7(BO_3)_3(SiO_4)$ X (X = Cl, Br)	$P6_3mc$	1.0 × KDP	Not reported	< 190	214
$Ba_3Ca_4(BO_3)_3(SiO_4)Cl$	$P6_3mc$	0.6 × KDP	Cal.0.03@1064 nm	＜190	215
Pb_2BO_3Cl	*P*321	9.0× KDP	Cal. 0.12@1064 nm	300	216
$Na_3Y(CO_3)_3$	*Ama*2	3.6 × KDP	Not reported	220	217
$Na_3Gd(CO_3)$	*Ama*2	3.5 × KDP	Not reported	223	217
$Na_4La_2(CO_3)_5$	$P6_3mc$	3.0 × KDP	Not reported	235	218
$CsNa_5Ca_5(CO_3)_8$	$P6_3mc$	1.0 × KDP	Not reported	210	218
$NaZnCO_3(OH)$	*Pc*	5.2 × KDP	Cal. 0.114@1064 nm	200	219
$LiZnCO_3(OH)$	$Pmn2_1$	3.2 × KDP	Cal. 0.147@1064 nm	190	220
$KSrCO_3F$	$P\bar{6}2m$	3.3 × KDP	Cal. 0.105@1064 nm	< 200	221
$RbSrCO_3F$	$P\bar{6}2m$	3.3 × KDP	Cal. 0.102@1064 nm	< 200	222
$KCaCO_3F$	$P\bar{6}2m$	3.6 × KDP	Cal. 0.112@1064 nm	< 200	223
$RbCaCO_3F$	$P\bar{6}2m$	1.1 × KDP	Cal. 0.116@1064 nm	< 200	223
$CsCaCO_3F$	$P\bar{6}2m$	1.1 × KDP	Cal. 0.107@1064 nm	< 200	223
$KMgCO_3F$	$P\bar{6}2m$	3.0 × KDP	Not reported	< 200	224
$RbMgCO_3F$	$P\bar{6}2m$	4.0 × KDP	Not reported	< 190	225
$Ca_2Na_3(CO_3)_3F$	*Cm*	3.0 × KDP	Exp. 0.082@589 nm	190	226
$Cs_3Ba_4(CO_3)_3F_5$	$P6_3mc$	1.2 × KDP	Not reported	210	227
$Cs_9Mg_6(CO_3)_8F_5$	$Pmn2_1$	0.5 × KDP	Not reported	208	228
$Na_8Lu_2(CO_3)_6F_2$	*Cc*	4.2 × KDP	Not reported	< 200	229
$Na_3Lu(CO_3)_2F_2$	*Cc*	4.2 × KDP	Not reported	< 200	229

$KCdCO_3F$	$P\bar{6}c2$	4.6 × KDP	Not reported	235	230
$RbCdCO_3F$	$P\bar{6}c2$	2.8 × KDP	Not reported	233	230
$CsPbCO_3F$	$P\bar{6}2m$	13.4× KDP	Not reported	300	231
$Y_8O(OH)_{15}(CO_3)_3Cl$	$P6_3$	2.5 × KDP	Cal. 0.074@1064 nm	235	232
$Ba_2(OH)_3NO_3$	$P\bar{6}2m$	4.0 × KDP	Exp. 0.080@532 nm	200	233
$Sr_2(OH)_3NO_3$	$P\bar{6}2m$	3.6 × KDP	Not reported	200	234
$La(OH)_2NO_3$	$P2_1$	5.0 × KDP	Not reported	260	235
$Y(OH)_2NO_3$	$P2_1$	5.5 × KDP	Not reported	257	235
$Gd(OH)_2NO_3$	$P2_1$	5.6 × KDP	Not reported	256	235
$Rb_2Na(NO_3)_3$	$Pmc2_1$	5.0 × KDP	Not reported	270	236
$La(IO_3)_2(NO_3)$	$P3_121$	0.6 × KDP	Not reported	290	237
$Sc(IO_3)_2(NO_3)$	$R32$	4.0 × KDP	Exp. 0.348@546 nm	298	238
$Pb_2(NO_3)_2(H_2O)F_2$	$Amm2$	12 × KDP	Cal. 0.23@1064 nm	300	239



(a) **(b)**

Figure S1. The single-crystals of $PbBe_2B_2O_6$ (a) before being soaked in distilled water, and (b) after being soaked in distilled water for two months.

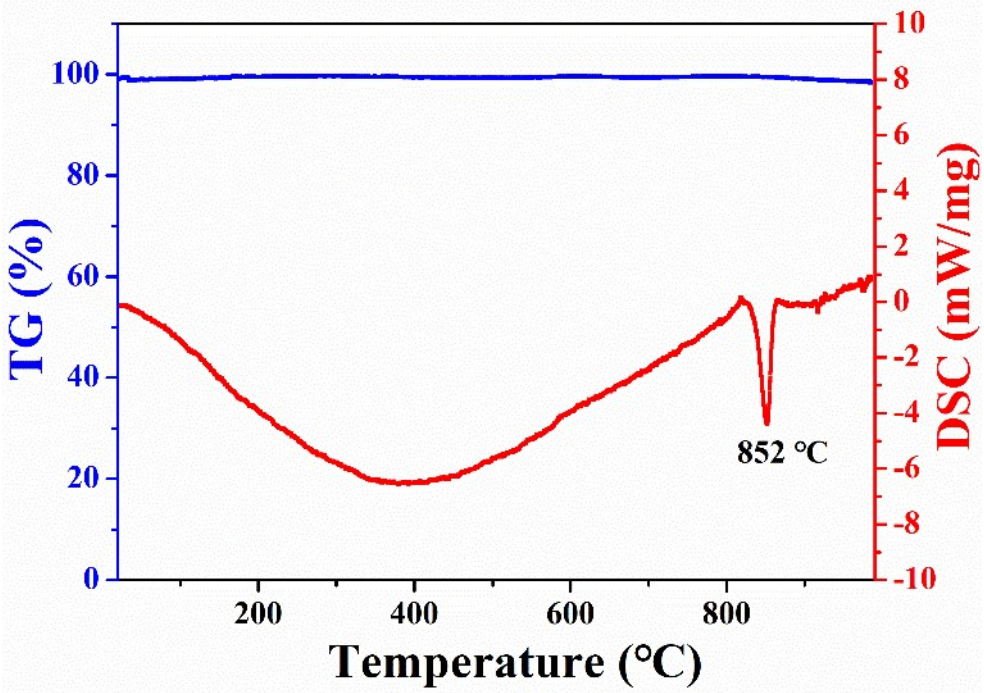


Figure S2. TG and DSC curves of $PbBe_2B_2O_6$.

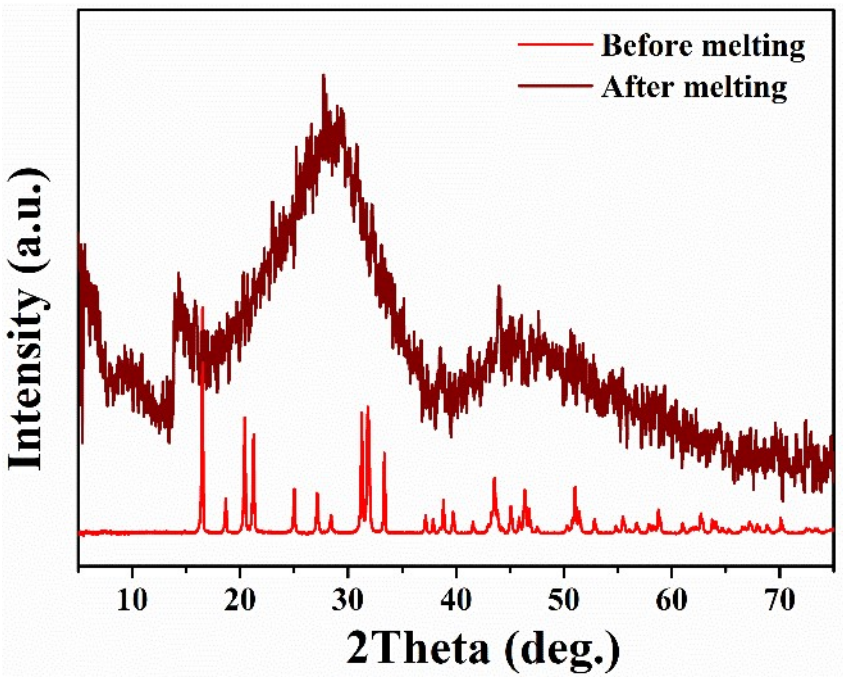


Figure S3. Powder XRD patterns of $PbBe_2B_2O_6$ before and after melting.

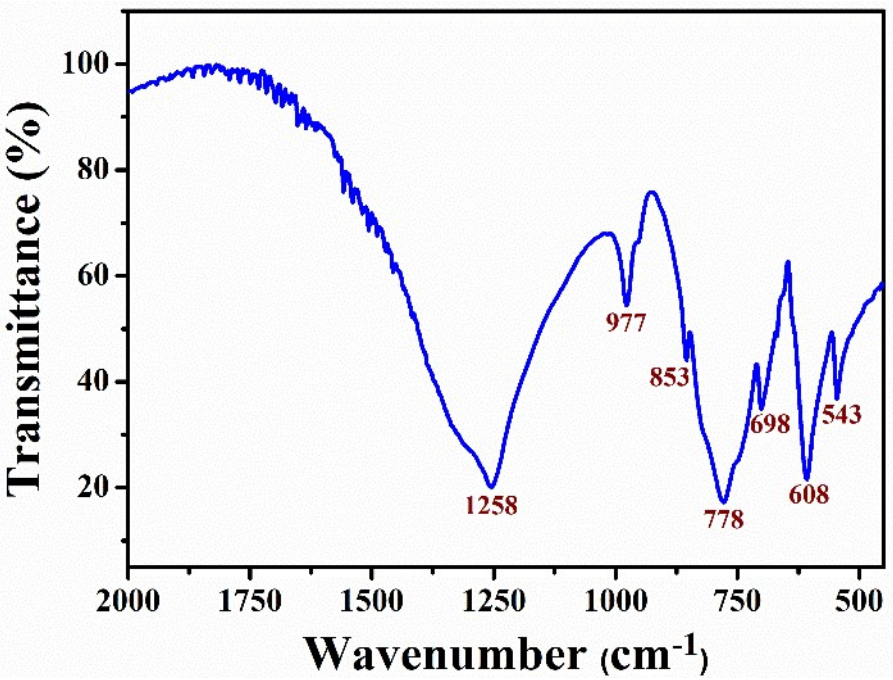


Figure S4. IR spectrum of $PbBe_2B_2O_6$.

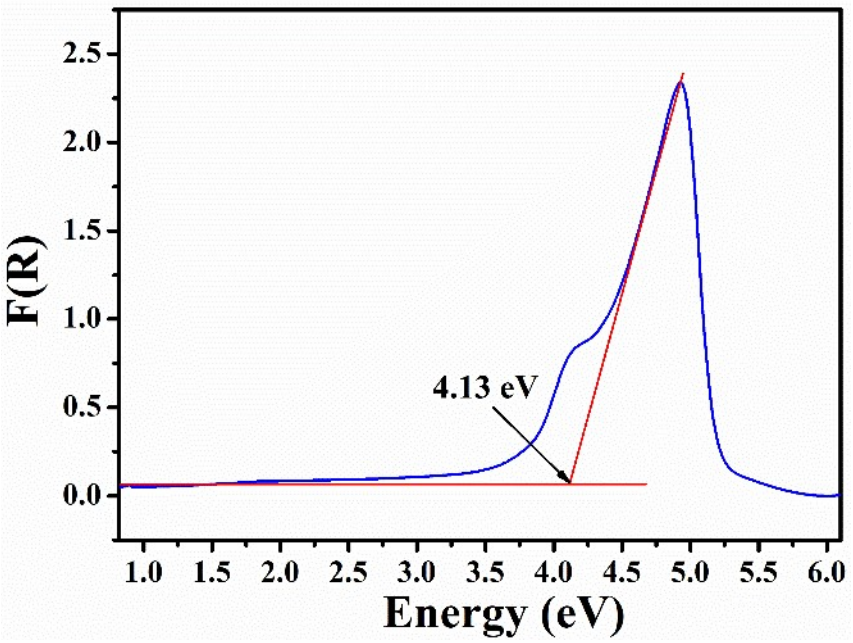


Figure S5. UV−visible−near-IR diffuse reflectance spectrum of $PbBe_2B_2O_6$.

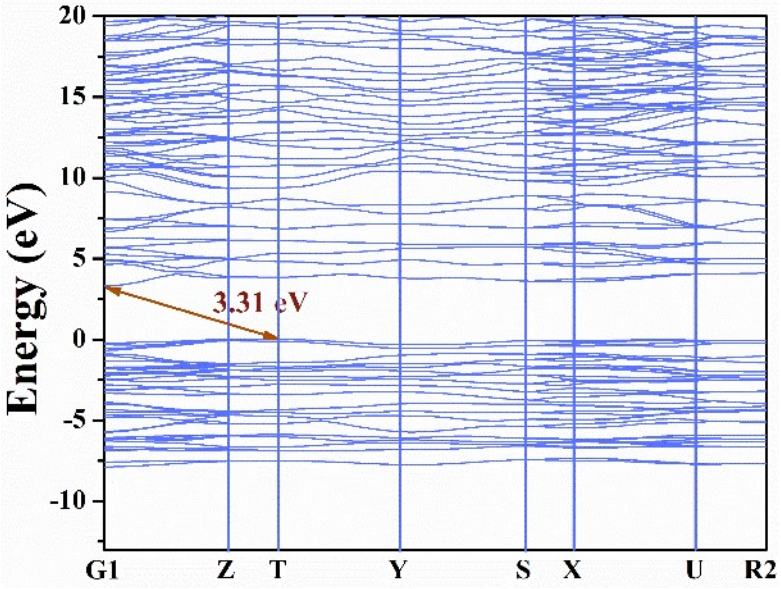


Figure S6. Electronic band structure of $PbBe_2B_2O_6$.

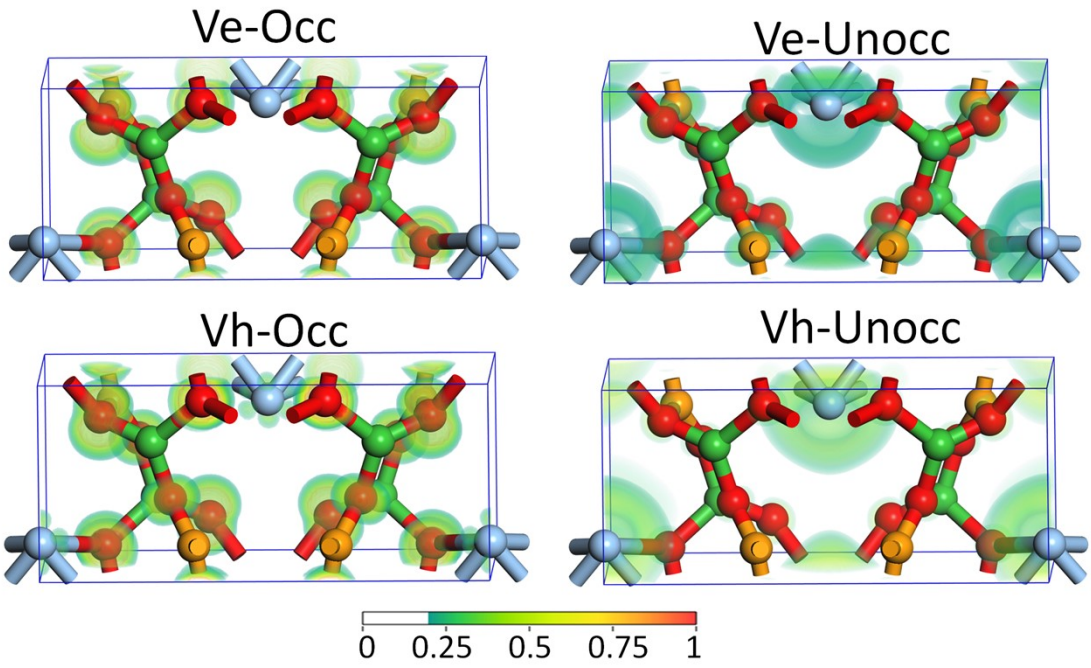


Figure S7. SHG-weighted electron density calculation of $PbBe_2B_2O_6$.

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