Supporting Information

Perfect Balance Harmony in Ba₂NO₃(OH)₃: A Beryllium-Free Nitrate as UV Nonlinear Optical Material

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1. Synthesis of Ba₂NO₃(OH)₃.

All starting materials Ba(NO₃)₂, Ba(OH)₂, and nitrogen were analytical grade from commercial sources and used without further treatment. Crystals of Ba₂NO₃(OH)₃ were synthesized via modified high-temperature solid state reactions in a self-made high-pressure apparatus by using Ba(OH)₂ as self-flux in a N₂ atmosphere at 10 MPa. A mixture of Ba(NO₃)₂ and Ba(OH)₂ at a molar ratio of Ba(NO₃)₂/Ba(OH)₂ = 1:4 were thoroughly ground with agate mortars and pestles and pressed into pellets, then loaded into platinum crucibles. The mixture (10 g) was heated in a programmable temperature electric furnace at 450 °C until the melt became transparent and clear. The homogenized melt solution was then cooled rapidly (50 °C/h) to the initial crystallization temperature (400 °C). It was further cooled slowly (2 °C/h) to the final crystallization temperature (350 °C) and then allowed to cool (30 °C/h) to room temperature. Colorless transparent sheet crystals of Ba₂NO₃(OH)₃ shown in Fig. S1 were obtained and washed with distilled water and dried in air. After proper structural analysis, pure powder samples of Ba₂NO₃(OH)₃ were obtained in quantitative yield through the solid-state reactions in a N₂ atmosphere from the stoichiometric mixtures of Ba(NO₃)₂ and Ba(OH)₂ at 350 °C for 2 days.

2. Instrumentations for physical property measurements.

Suitable single crystals were selected under an optical microscope. The intensity data were collected on a Bruker SMART BREEZE diffractometer with graphite-monochromated MoK_a radiation(λ =0.71073Å) at room temperature. All absorption corrections were per-formed by using the SADABS program. The structure was solved by direct methods and refined by full-matrix least squares on *F*² using the SHELX-2014 program package^[1,2]. All of the structures were verified using the ADDSYM algorithm from the program PLATON and no higher symmetries were found.^[3] All hydrogen atoms were located geometrically or in a difference Fourier map, and refined with a riding model. IR spectra (KBr pellets) were recorded on a Vertex 70 Fourier transform infrared spectrometer. Thermal analyses were performed in a dynamic nitrogen atmosphere using a Netzsch STA 409 PC thermal analyzer, and with a heating rate of 10 °C/min and in the range of 100-800 °C. Powder XRD patterns were obtained using a Rigaku Smartlab powder X-ray diffractometer with CuK α radiation (λ = 1.54056 Å), in the angular range of 20 = 5-70°, and with a scan step width of 0.05° and a fixed time of 0.2 s. The UV transmittance spectroscopy was recorded at room temperature using a PerkinElmer Lamda-950

UV/vis/NIR spectrophotometer in the range of 200-2500nm, and the absorption (K/S) data were calculated from the Kubelka-Munk function^[4]. A crystal with dimensions of $\sim 5 \text{ mm} \times \sim 3 \text{ mm} \times \sim 1 \text{ mm}$ was used for the measurement without polishing. The birefringence was measured on a Nikon ECLIPSE LV100 POL polarizing microscope. The wavelength of the light source was 589.6 nm. The formula of the calculated birefringence can be expressed as follows: $\triangle R$ (retardation) = $\triangle n \times T$, where $\triangle R$ denotes the optical path difference, $\triangle n$ represents birefringence, and T denotes the thickness of the crystal. Powder second-harmonic generation (SHG) signals were measured using the method adapted from Kurtz and Perry^[5]. Since SHG efficiencies are known to depend strongly on particle size, polycrystalline samples were ground and sieved into the following particle size ranges: 25-45, 45-62, 62-75, 75-109, 109-150 and 150-212 µm. The measurements were performed with a Q-switched Nd:YAG laser at 1064 nm and a frequency doubling at 532 nm, for visible and UV SHG, respectively. To make relevant comparisons with known NLO materials, crystalline KDP and BBO were also ground and sieved into the same particle size ranges and used as the references for visible and UV SHG, respectively. The samples were pressed between glass microscope cover slides and secured with tape in 1-mm thick aluminum holders containing an 8-mm diameter hole. They were then placed in a light-tight box and irradiated with a pulsed laser. A cutoff filter was used to limit background flash-lamp light on the sample, and an interference filter was used to select the second harmonic for detection with a photomultiplier tube attached to a RIGOL DS1052E 50-MHz oscilloscope. This procedure was then repeated using the standard nonlinear optical materials KDP and BBO, and the ratio of the second-harmonic intensity outputs was calculated. No index-matching fluid was used in any of the experiments.

3. Theoretical calculation.

3.1 optical properties calculation.

Our ab initio calculations for compound Ba₂NO₃(OH)₃ were performed using the full-potential projector augmented wave (PAW) method^[6], as implemented in the Vienna ab initio Simulation Package (VASP) package^[7-10]. The exchange-correlation (XC) interaction was treated by the Perdew-Burke-Ernaerhof (GGA-PBE)^[11] functional. The valence electrons of the component elements were treated as H 1s¹, O 2s²2p⁴, N 2s²2p³, Ba $5s^25p^66s^2$. Hydrogen atomic positions of the OH⁻ groups were obtained by fixed-lattice constant optimization based on the X-ray crystal structure. A Γ -centered $9 \times 9 \times 7$ Monkhorst-Pack grid for the Brillouin zone sampling^[12] and a cutoff energy of 550 eV for the plane wave expansion were found to get convergent lattice parameters. In geometry optimizations, all the atomic positions and lattice constants were fully relaxed until the quantum mechanical forces became less than 0.01 eV/Å, and the total energy was converged to 0.1 meV.

To obtain the linear optical properties, the complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ has been determined in the random phase approximation from the PBE wavefunctions. The imaginary part of the dielectric function due to direct inter-band transitions is given by the expression,

$$\varepsilon_{2}(\mathbf{h}\omega) = \frac{2e^{2}\pi}{\Omega\varepsilon_{0}} \sum_{k,v,c} \left| \left\langle \psi_{k}^{c} \left| u \cdot r \right| \psi_{k}^{v} \right\rangle \right|^{2} \delta(E_{k}^{c} - E_{k}^{v} - E),$$

where Ω , ω , u, v and c are the unit-cell volume, photon frequencies, the vector defining the polarization of the incident electric field, valence and conduction bands, respectively. The real part of the dielectric function is obtained from ε_2 by a Kramers-Kronig transformation,

$$\varepsilon_1(\omega) = 1 + (\frac{2}{\pi}) \int_0^{+\infty} d\omega' \frac{\omega'^2 \varepsilon_2(\omega)}{\omega'^2 - \omega^2},$$

In calculation of the static $\chi^{(2)}$ coefficients, the so-called length-gauge formalism derived by Aversa and Sipe^[7] and modified by Rashkeev *et al*^[13] is adopted, which has been proved to be successful in calculating the second order susceptibility for semiconductors and insulators.^[14-17] In the static case, the imaginary part of the static second-order optical susceptibility can be expressed as:

$$\begin{aligned} \chi^{abc} \\ &= \frac{e^3}{h^2 \Omega} \sum_{nml,k} \frac{r_{nm}^a (r_{ml}^b r_{ln}^c + r_{ml}^c r_{ln}^b)}{2\omega_{nm} \omega_{ml} \omega_{ln}} [\omega_n f_{ml} + \omega_m f_{ln} + \omega_l f_{nm}] \\ &+ \frac{ie^3}{4h^2 \Omega} \sum_{nm,k} \frac{f_{nm}}{\omega_{mn}^2} [r_{nm}^a (r_{mn;c}^b + r_{mn;b}^c) + r_{nm}^b (r_{mn;c}^a + r_{mn;a}^c) + r_{nm}^c (r_{mn;b}^a + r_{mn;a}^b)] \end{aligned}$$

where *r* is the position operator, $\hbar\omega_{nm} = \hbar\omega_n - \hbar\omega_m$ is the energy difference for the bands *m* and *n*, $f_{mn} = f_m - f_n$ is the difference of the Fermi distribution functions, subscripts *a*, *b*, and *c* are Cartesian indices, and $r^b_{mn;a}$ is the

so-called generalized derivative of the coordinate operator in k space,

$$r_{nm;a}^{b} = \frac{r_{nm}^{a}\Delta_{mn}^{b} + r_{nm}^{b}\Delta_{mn}^{a}}{\omega_{nm}} + \frac{i}{\omega_{nm}} \times \sum_{l} (\omega_{lm}r_{nl}^{a}r_{lm}^{b} - \omega_{nl}r_{nl}^{b}r_{lm}^{a}),$$

where $\Delta^{a}_{nm} = (p^{a}_{nn} - p^{a}_{mm}) / m$ is the difference between the electronic velocities at the bands *n* and *m*.

3.2 Adsorption energy of foreign water molecules calculation.

Here, the adsorption energy of a foreign water molecule in $Ba_2NO_3(OH)_3$, and $Ba(OH)_2$ crystal cells were calculated. All calculations based on density functional theory (DFT) were carried out using the CASTEP package ^[18] implemented in the Material Studio program. The exchange-correlation contribution to the total electronic energy was treated with generalized gradient approximation (GGA) in the form of Perdew–Burke–Ernzerhof (PBE). A kinetic energy cutoff of 400 eV was used along with ultrasoft pseudopotentials ^[19]. The criteria of convergences of energy, force, and displacement are set as 2×10^{-5} eV/atom, 0.05 eV/Å, and 0.002 Å, respectively.

First of all, we carried out the optimizations of $Ba_2NO_3(OH)_3$, and $Ba(OH)_2$ crystal cells. Here, relaxation of both lattice parameters and atomic coordinates was applied. The Brillouin zone was sampled using Monkhors-Pack mesh with 2×2×3, and 1×1×2 for $Ba_2NO_3(OH)_3$, and $Ba(OH)_2$. The calculated lattice parameters were shown in Table S4, which is within 4% difference compared with experimental values.

Then, a foreign water molecule was introduced into crystal cells. Different adsorption sites were considered. The coordinates were fully relaxed with the cell size fixed. The most stable configurations of relaxed water/cell adducts were hereafter named $Ba_2NO_3(OH)_3$ -w, and $Ba(OH)_2$ -w. The adsorption energy ΔE_{ads} was calculated according to the following expression:

 $\Delta E_{ads} = E_{cell + water} - (E_{cell} + E_{water})$

where E_{water} is the energy of gaseous water molecule, E_{bulk} is the energy of a relaxed crystal cell, and $E_{cell+water}$ is the minimized total energy of the adsorption systems. Negative adsorption energies denote an exothermic adsorption process.

In our simulations, water molecule dissociates in $Ba_2NO_3(OH)_3$ lattice. As shown in Fig. S9-(a), a proton transfer in which water acts as proton donor occurred between the OH group of $Ba_2NO_3(OH)_3$ and the foreign

H₂O. In the meantime, a H-bond is established between the remaining water OH⁻ and a nitrate group (NO...HO distance of 1.791 Å). The plane structure, consisting of nitrate and barium ions, is broken. Such deformation balances the favorable interactions established through water dissociation, which leads to an endothermic process with $\Delta E_{ads} = 865.89$ meV. Thereupon, the dense matrix of Ba₂NO₃(OH)₃ may not allow the incoming of water molecule, which results in the insolubility of Ba₂NO₃(OH)₃.

On the other hand, $Ba(OH)_2$ -w appears quite stable as for hydrogen bond interactions. As we can see in Fig. S9-(b), the foreign H₂O comes into the interstice of Ba(OH)₂. The water hydrogens are engaged in two hydrogen bonds with near OH groups (HO-H...O distances of 1.491 Å and 1.487 Å). The water oxygen also remains contact with another OH through a relatively weak hydrogen bond (1.811 Å). This result clearly shows that a water molecule is stable in Ba(OH)₂. Such insertion process is characterized by an exothermic energy ($\Delta E_{ads} = -691.86$ meV).

4. Tables and Figures

Formula	Ba ₂ NO ₃ (OH) ₃
Formula Mass (amu)	387.71
Crystal System	Hexagonal
Space Group	P2m
a (Å)	6.9069 (3)
c (Å)	3.8028(4)
α(°)	90
γ(°)	120
V(Å ³)	157.11(2)
Z	1
ρ (calcd) (g/cm ³)	3.562
Temperature (K)	293(2)
λ(Å)	0.71073
F(000)	170
μ (mm ⁻¹)	12.42
Final R indices (I> 2σ (I))a R ₁ /wR ₂	0.005/0.013
GOF on F ²	0.97
Absolute Structure Parameter	-0.03(4)
$ \Sigma_1(F) = \Sigma F_0 - F_c / \Sigma F_0 $. wR ₂ (F ₀ ²) = $[\Sigma w (F_0^2 - F_c^2)^2 / \Sigma w (F_0^2)^2]^1$	/2.

Table S1. Crystal Data and Structure Refinement for Ba₂NO₃(OH)₃.^a

	x	у	Ζ	$U_{eq}(Å^2)$	BVS
Bal	0.3333	0.6667	0.0000	0.00369 (10)	2.04
N1	0.0000	0.0000	0.0000	0.0006 (7)	5.03
01	0.1796 (4)	0.1796 (4)	0.0000	0.0186 (6)	1.98
O2	0.4486 (3)	1.0000	-0.5000	0.0064 (5)	1.06
H1	0.331 (3)	1.0000	-0.5000	0.010*	

Table S2. Atomic coordinates and equivalent isotropic displacement parameters for $Ba_2NO_3(OH)_3$. $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

 Table S3. Selected Bond lengths (Å) and angles (deg) for Ba₂NO₃(OH)₃.

Ba1—O2 ⁱ	2.7779 (3)	Ba1—Ba1 ^{vi}	3.8028 (4)
Ba1—O2 ⁱⁱ	2.7779 (3)	Ba1—Ba1 ^{vii}	3.9877 (2)
Ba1—O2	2.7779 (3)	01—N1	1.241 (2)
Ba1—O2 ⁱⁱⁱ	2.7779 (3)	O1—Ba1 ^{viii}	2.9785 (18)
Ba1—O2 ^{iv}	2.7779 (3)	N1—O1 ^{ix}	1.241 (2)
Ba1—O2 ^v	2.7779 (3)	N1—O1 ^x	1.241 (2)
Ba1—O1 ^v	2.9785 (19)	O2—Ba1 ^{vi}	2.7779 (3)
Ba1—O1 ⁱⁱ	2.9785 (19)	O2—Ba1 ^{xi}	2.7779 (3)
Ba1—O1	2.9785 (19)	O2—Ba1 ^{xii}	2.7779 (3)
O2 ⁱ —Ba1—O2 ⁱⁱ	137.244 (4)	O2 ⁱⁱⁱ —Ba1—Ba1 ⁱ	46.806 (6)
O2 ⁱ —Ba1—O2	86.388 (12)	O2 ^{iv} —Ba1—Ba1 ⁱ	46.806 (6)
O2 ⁱⁱ —Ba1—O2	78.302 (9)	O2 ^v —Ba1—Ba1 ⁱ	133.194 (6)
O2 ⁱ —Ba1—O2 ⁱⁱⁱ	78.302 (9)	O1 ^v —Ba1—Ba1 ⁱ	90.0
O2 ⁱⁱ —Ba1—O2 ⁱⁱⁱ	86.388 (12)	Ol ⁱⁱ —Bal—Bal ⁱ	90.0
O2 ⁱⁱⁱ —Ba1—O2 ^{iv}	78.302 (9)	O2 ⁱⁱⁱ —Ba1—Ba1vi	133.194 (6)
O2 ⁱ —Ba1—O2 ^v	137.244 (5)	O2 ^{iv} —Ba1—Ba1 ^{vi}	133.194 (6)
O2 ⁱⁱ —Ba1—O2 ^v	78.302 (9)	O2v—Ba1—Ba1vi	46.806 (6)
O2—Ba1—O2 ^v	78.302 (9)	O1 ^v —Ba1—Ba1 ^{vi}	90.0
O2 ⁱⁱⁱ —Ba1—O2 ^v	137.244 (4)	O1 ⁱⁱ —Ba1—Ba1 ^{vi}	90.0
O2 ^{iv} —Ba1—O2 ^v	86.388 (12)	O1—Ba1—Ba1 ^{vi}	90.0
O2 ⁱ —Ba1—O1 ^v	69.93 (5)	Ba1 ⁱ —Ba1—Ba1 ^{vi}	180.0
O2 ⁱⁱ —Ba1—O1 ^v	67.32 (4)	O2 ⁱ —Ba1—Ba1 ^{vii}	104.37 (4)
O2—Ba1—O1 ^v	69.93 (5)	O2 ⁱⁱ —Ba1—Ba1 ^{vii}	44.131 (6)

O2 ⁱⁱⁱ —Ba1—O1 ^v	67.32 (4)	O2—Ba1—Ba1 ^{vii}	104.37 (4)
O2 ^{iv} —Ba1—O1 ^v	136.771 (8)	O2 ⁱⁱⁱ —Ba1—Ba1 ^{vii}	44.131 (6)
O2 ^v —Ba1—O1 ^v	136.771 (8)	O2 ^{iv} —Ba1—Ba1 ^{vii}	118.01 (4)
O2 ⁱ —Ba1—O1 ⁱⁱ	67.32 (4)	O2 ^v —Ba1—Ba1 ^{vii}	118.01 (4)
O2 ⁱⁱ —Ba1—O1 ⁱⁱ	136.771 (8)	O1v—Ba1—Ba1vii	47.98 (3)
O2—Ba1—O1 ⁱⁱ	67.32 (4)	O1 ⁱⁱ —Ba1—Ba1 ^{vii}	167.98 (3)
O2 ⁱⁱⁱ —Ba1—O1 ⁱⁱ	136.771 (8)	O1—Ba1—Ba1 ^{vii}	72.02 (3)
O2 ^{iv} —Ba1—O1 ⁱⁱ	69.93 (5)	Ba1 ⁱ —Ba1—Ba1 ^{vii}	90.0
O2 ^v —Ba1—O1 ⁱⁱ	69.93 (5)	Ba1vi—Ba1—Ba1vii	90.0
O1v—Ba1—O1 ⁱⁱ	120.0	N1—O1—Ba1 ^{viii}	137.98 (3)
O2 ⁱ —Ba1—O1	136.771 (8)	N1—O1—Ba1	137.98 (3)
O2 ⁱⁱ —Ba1—O1	69.93 (5)	Ba1 ^{viii} —O1—Ba1	84.04 (6)
O2—Ba1—O1	136.771 (8)	01—N1—01 ^{ix}	120.0
O2 ⁱⁱⁱ —Ba1—O1	69.93 (5)	01—N1—01 ^x	120.0
O2 ^{iv} —Ba1—O1	67.32 (4)	O1 ^{ix} —N1—O1 ^x	120.0
O2 ^v —Ba1—O1	67.32 (4)	Ba1 ^{vi} —O2—Ba1 ^{xi}	165.32 (8)
O1 ^v —Ba1—O1	120.0	Ba1 ^{vi} —O2—Ba1	86.388 (12)
O1 ⁱⁱ —Ba1—O1	120.0	Ba1 ^{xi} —O2—Ba1	91.738 (12)

Symmetry codes: (i) *x*, *y*, *z*+1; (ii) -*y*+1, *x*-*y*+1, *z*; (iii) -*y*+1, *x*-*y*+1, *z*+1; (iv) -*x*+*y*, -*x*+1, *z*+1; (v) -*x*+*y*, -*x*+1, *z*; (vi) *x*, *y*, *z*-1; (vii) *y*-1, *x*, -*z*; (viii) *y*, *x*, -*z*; (ix) -*y*, *x*-*y*, *z*; (x) -*x*+*y*, -*x*, *z*; (xi) *y*, *x*+1, -*z*; (xii) *y*, *x*+1, -*z*-1.

		lattice parameters			ΔE_{ads}
	a(Å)	b(Å)	c(Å)	a, b, c (degree)	(meV)
Ba ₂ (OH) ₃ NO ₃	7.10	7.10	3.86	90.00 90.00 120.00	865.89
$Ba(OH)_2$	11.41	16.79	7.19	90.00 90.00 90.00	-691.86

Table S4. Relaxed crystal structure information and the water adsorption energies ΔE_{ads} for Ba₂(OH)₃NO₃, and Ba(OH)₂.

Table S5. Optical Properties of UV NLO Crystals.

Crystals	Birefringence (Δn)	SHG coefficient (×KDP)	absorption edge (nm)
Ba ₂ NO ₃ (OH) ₃	0.080	4.0	<200
Bi ₃ TeO ₆ OH(NO ₃) ₂	0.115	3.0	345
$La(OH)_2NO_3$	0.146	5.0	260
KBBF	0.077	1.0	147
LiB ₃ O ₅ (LBO)	0.043	2.0	150
β -BaB ₂ O ₄ (BBO)	0.125	5.8	185
$Li_4Sr(BO_3)_2$	0.056	2.0	186
KSrCO ₃ F	0.105	3.0	195

Crystals	SHG coefficient (×KDP)	structural criterion C	densities of [NO ₃] (n/V) (Å ⁻³)	(n/V)×C (Å ⁻³)
Ba ₂ NO ₃ (OH) ₃	4.0	1.00	0.0065	0.0065
$[Pb_4(OH)_4](NO_3)_4$	0.7	0.17	0.0109	0.0018
$[LaPb_8O(OH)_{10}(H_2O)](NO$	1.3	0.32	0.0087	0.0028
3)7				
$La(OH)_2NO_3$	5.0	0.81	0.0101	0.0081



Fig. S1. Photograph of Ba₂NO₃(OH)₃ crystals.



Fig. S2. Calculated and experimental powder X-ray diffraction (PXRD) patterns for Ba₂NO₃(OH)₃. The black curve is the calculated one obtained from single crystal X-ray structure analyse, the red is the experimental one for pure phase, the blue is the experimental one for the sample exposed under humid air for 3 months.



Fig. S3. Oscilloscope traces of SHG signals for $Ba_2NO_3(OH)_3$ and $Ba_2NO_3(OH)_3$ ' (after being exposed under humid air at room temperature for 3 months), the SHG intensity is almost unchanged. KDP sieved in the same particle sizes was used as the reference.



Fig. S4. TGA-DSC spectrum for Ba₂NO₃(OH)₃.



Fig. S5. IR spectrum for Ba₂NO₃(OH)₃.



Fig. S6. UV transmittance spectroscopy for Ba₂NO₃(OH)₃.



Fig. S7. Calculated band structure of $Ba_2NO_3(OH)_3$ (the Fermi level is set at 0 eV).



Fig. S8. Calculated refractive indexes for Ba₂NO₃(OH)₃.



Fig. S9. Water molecule dissociates in $Ba_2(OH)_3NO_3$ (a) and $Ba(OH)_2$ (b) lattice.

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