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Alkali metal-alkaline earth metal borate crystal $\text{LiBa}_3(\text{OH})(\text{B}_9\text{O}_{16})[\text{B}(\text{OH})_4]$ as a new deep-UV nonlinear optical material†

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A new noncentrosymmetric alkali metal-alkaline earth metal borate with the formula $\text{LiBa}_3(\text{OH})(\text{B}_9\text{O}_{16})[\text{B}(\text{OH})_4]$ has been synthesized using a convenient hydrothermal method. The structure features a three-dimensional zeolite-like framework and consists of a $[\text{B}_9\text{O}_{19}(\text{OH})]^{12-}$ primary building unit with 6-membered-ring channels along the *c*-axis. The Ba dications and $[\text{B}(\text{OH})_4]^-$ anions are encapsulated in the 6-membered-ring channels, while the Li cations are located between two adjacent $[\text{B}_9\text{O}_{19}(\text{OH})]^{12-}$ clusters. Second-harmonic generation (SHG) measurements show that $\text{LiBa}_3(\text{OH})(\text{B}_9\text{O}_{16})[\text{B}(\text{OH})_4]$ is type-I phase-matching, with SHG response ca. 1.2 times that of KH_2PO_4 . In addition, it exhibits a wide transparency range with a short UV cut-off edge (< 200 nm), suggesting that $\text{LiBa}_3(\text{OH})(\text{B}_9\text{O}_{16})[\text{B}(\text{OH})_4]$ is a potential deep-UV nonlinear optical material. Density functional theory calculations were employed to rationalize the band structure and density of states as well as the electron density.

Introduction

Deep-ultraviolet (UV) nonlinear optical (NLO) crystals can produce coherent light at wavelengths $\lambda < 200$ nm, and are therefore of enormous interest for practical applications in semiconductor lithography, nano-micro mechanical machining, and biological gene engineering.^{1–4} The best candidates thus far for UV and deep-UV NLO materials are primarily metal borates,⁵ metal phosphonates,⁶ and metal carbonates.⁷ For example, β - BaB_2O_4 (BBO),⁸ $\text{RbBa}_2(\text{PO}_3)_5$,⁹ $\text{Na}_8\text{Lu}_2(\text{CO}_3)_6\text{F}_2$ and $\text{Na}_3\text{Lu}(\text{CO}_3)_2\text{F}_2$ ¹⁰ exhibit large powder second-harmonic generation (SHG) signals of ca. 6.0, 1.4, 4.3 and 4.2 times that of KH_2PO_4 (KDP), respectively. New UV and deep-UV NLO materials are still dominated by metal borates due to their relatively high optical damage threshold, wide ultraviolet transmittance and rich array of structures.¹¹ Among the reported borates, $\text{KBe}_2\text{BO}_3\text{F}_2$ (KBBF) is the only practically applicable deep-UV NLO crystal, but it is difficult to grow large crystals due to the weak interlayer K-F ionic bonds.¹² In order to enhance the interlayer bonding strength, other beryllium-containing deep-UV NLO borates, such as $\text{Na}_2\text{CsBe}_6\text{B}_5\text{O}_{15}$ ($1.2 \times \text{KDP}$, $\lambda < 200$ nm),¹³ $\text{NaSr}_3\text{Be}_3\text{B}_3\text{O}_9\text{F}_4$ ($4.0 \times \text{KDP}$, $\lambda < 170$ nm),¹⁴ and $\text{NaCaBe}_2\text{B}_2\text{O}_6\text{F}$ ($0.3 \times \text{KDP}$, $\lambda < 190$ nm)¹⁵ as well as $\text{Na}_2\text{Be}_4\text{B}_4\text{O}_{11}$ ($1.3 \times \text{KDP}$, $\lambda < 171$ nm) and $\text{LiNa}_5\text{Be}_{12}\text{B}_{12}\text{O}_{33}$ ($1.4 \times \text{KDP}$, $\lambda < 169$ nm),¹⁶ have been prepared. However, the high toxicity of beryllium severely limits their practical application.

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†Electronic Supplementary Information (ESI) available: photographs, X-ray crystallographic information files, IR spectra, UV-Vis-NIR diffuse reflectance spectra, experimental and simulated powder X-ray diffraction patterns, thermogravimetric analyses, and density of states (DOS) are available for $\text{LiBa}_3(\text{OH})(\text{B}_9\text{O}_{16})[\text{B}(\text{OH})_4]$. CCDC 1476577. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

Despite the requirements for high SHG coefficients and a wide transparency range in a useful material, large band-gap materials usually possess small NLO coefficients,¹⁷ and it is difficult to balance these conflicting factors. One effective strategy is to introduce alkali metal, alkaline-earth metal, or fluoride ions, all of which may lead to a blue shift in the UV cutoff edge, and thereby potentially afford promising UV or deep-UV NLO materials. Alkali metal and alkaline-earth metal borates, in particular, possess relatively wide UV transparencies extending into the deep-UV region because there are no d-d or f-f electronic transitions.¹⁸ However, these metal borate NLO crystals are invariably isolated by high-temperature solid-state methods;^{13–16,19} to the best of our knowledge, there are no data regarding the deep-UV NLO properties of alkali metal-alkaline earth metal borates synthesized under mild hydrothermal conditions. We report herein the facile hydrothermal synthesis of an interesting noncentrosymmetric (NCS) alkali metal-alkaline earth metal borate $\text{LiBa}_3(\text{OH})(\text{B}_9\text{O}_{16})[\text{B}(\text{OH})_4]$ (1), single-crystal structural studies, UV-Vis-NIR diffuse reflectance spectroscopy studies, and studies showing promising deep-UV NLO behavior with a moderate SHG response (1.2 times that of KDP), together with theoretical calculations exploring the band structure and density of states as well as the electron density.

Experimental

Reagents

All reagents including $\text{Ba}(\text{NO}_3)_2$ (99.5%), $\text{Li}_2\text{B}_4\text{O}_7$ (99.99%) and **KF** (99.5%) were purchased commercially and used without further purification.

Synthesis

A mixture of $\text{Ba}(\text{NO}_3)_2$ (0.261 g, 1.00 mmol), **KF** (0.021 g, 0.50 mmol), and $\text{Li}_2\text{B}_4\text{O}_7$ (0.169 g, 1.00 mmol) in deionized water (10 mL) was placed in a 20 mL Teflon-lined stainless steel autoclave. After stirring for 30 min, the autoclave was

sealed, heated at 210 °C for 72 h, and then slowly cooled to room temperature at a rate of 4 °C/h. The initial and final pH values were 8.4 and 8.0, respectively. Colorless needle-like crystals of $\text{LiBa}_3(\text{OH})(\text{B}_9\text{O}_{16})[\text{B}(\text{OH})_4]$ were collected and dried in air (Fig. S1 in the ESI†). Yield: 72% (based on Ba). The synthesis of **1** depends on exercising subtle control over various hydrothermal parameters, especially pH, which may perform an important role in promoting the formation of the tetrahydroxyborate ion: $\text{B}_4\text{O}_7^{2-} + 7\text{H}_2\text{O} = 2\text{H}_3\text{BO}_3 + 2\text{B}(\text{OH})_4^-$. Compound **1** shows good chemical stability, remaining stable in air over a period of several months.

Structural Determination

The crystal structure determination of **1** was performed on a Bruker D8 VENTURE CMOS X-ray diffractometer equipped with a graphite monochromator affording $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. Data collection and reduction were performed using APEX II software. Multi-scan absorption correction was applied to the data set using the APEX II program. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares using the *SHELXTL-97* software package.²⁰ All non-hydrogen atoms were refined with anisotropic displacement parameters. The $U(\text{eq})$ of the O(9) atom in **1** appeared to be very high. Consequently, the O(9) occupancy was refined, converging to 0.33. The disorder of oxygen atom O(8) in **1** resulted in a large thermal ellipsoid, which was modelled by two 50% parts, atoms O(8) and O(8)A. All hydrogen atoms are located at geometrically calculated positions and refined with isotropic thermal parameters. Atoms O(5), O(8) and O(9) are assigned to hydroxyl groups according to the requirement of charge balance. The refined Flack factor is 0.03(3), which is close to zero, confirming the correctness of the absolute structure. Using PLATON, the structure was also checked for possible missing symmetry, none being found.²¹ Crystal data and structure refinement information of the compound are summarized in Table 1. Selected important bond distances ($\text{\AA}$) and angles (deg) are listed in Table S1 (ESI†).

IR Spectrum

The FT-IR spectrum of **1** was measured with a Nicolet 360 FT-IR instrument (KBr discs) in the range 500–4000 cm^{-1} .

UV-Vis-NIR Diffuse Reflectance Spectrum

The optical diffuse-reflectance spectrum was obtained with a UV-3600 Plus UV-Vis-NIR spectrophotometer at room temperature. A BaSO_4 plate was used as a standard (100% reflectance). The absorption spectrum was calculated from the reflectance spectrum using the Kubelka-Munk function $\alpha/S = (1 - R)^2/2R$, where α is the absorption coefficient, S is the scattering coefficient that is practically wavelength-independent when the particle size is larger than 5 μm , and R is the reflectance.²²

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) experiments were carried out on a TGA/1100SF instrument at a heating rate of 10 °C/min under a nitrogen atmosphere.

Powder X-ray Diffraction

The powder X-ray diffraction (P-XRD) pattern was recorded using $\text{Cu-K}\alpha$ radiation on a Bruker D8 X-ray diffractometer in the angular range $2\theta = 5\text{--}70^\circ$ with a step size of 0.02° and a fixed time of 1s/step.

Second-Order NLO Measurements

Measurements of the powder frequency-doubling effect were carried out by the method of Kurtz and Perry,²³ employing a Q-switched Nd:YAG laser at 1064 nm and frequency doubling to 532 nm for visible and ultraviolet SHG, respectively. The crystal samples were ground and sieved into six distinct particle size ranges (10–26, 26–50, 50–74, 74–150, 150–200 and 200–280 μm) to check whether or not they were phase-matchable. The samples were pressed into disks with diameters of 6 mm that were placed between glass microscope slides and secured with tape in a 1 mm thick aluminum holder. Sieved KDP and BBO samples (10–26, 26–50, 50–74, 74–150, 150–200 and 200–280 μm) were used as references for the SHG signals.

Computational Method

All electronic structure calculations were performed using the VASP code²⁴ in the framework of density functional theory (DFT). The general gradient approximation (GGA) function of Perdew-Burke-Ernzerhof (PBE)²⁵ was employed. A plane wave

Table 1 Crystal data and structure refinement for **1**^a

Empirical formula	$\text{LiBa}_3(\text{OH})(\text{B}_9\text{O}_{16})[\text{B}(\text{OH})_4]$
Formula weight	868.07
Temperature (K)	293(2)
Crystal system	trigonal
Space group	$P31c$ (no. 159)
a ($\text{\AA}$)	10.1984(3)
b ($\text{\AA}$)	10.1984(3)
c ($\text{\AA}$)	8.7126(4)
α ($^\circ$)	90
β ($^\circ$)	90
γ ($^\circ$)	120
Volume ($\text{\AA}^3$)	784.77(5)
Z	2
Density (calculated) ($\text{g}\cdot\text{cm}^{-3}$)	3.674
Absorption coefficient (mm^{-1})	7.570
$F(000)$	788
Theta range for data collection ($^\circ$)	3.28–27.46
Limiting indices	$-13 \leq h \leq 13$, $-12 \leq k \leq 13$, $11 \leq l \leq 11$
R_{int}	0.0343
Reflections collected / unique	6617 / 1206
Goodness-of-fit on F^2	1.130
Final R indices [$F_o^2 > 2\sigma(F_o^2)$] ^a	0.0201/0.0455
R indices (all data) ^a	0.0214/0.0456
Largest diff. peak and hole ($\text{e \AA}^{-3}$)	0.624 and -0.922

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

basis set with a frozen-core projector-augmented wave (PAW)²⁶ potential and a plane wave cut off energy of 520 was used for **1**. A dense k grid of $6 \times 6 \times 8$ was employed in the calculation of density of states (DOS). The second-order nonlinear optical susceptibilities were obtained based on the sum-over-states approach. Because of the underestimation of DFT band gaps, the scissor operation was applied to the optical property calculations. A total 288 k-points in the full Brillouin zone and 100 unoccupied bands were applied to generate the momentum matrix elements, which were used in the later SHG calculations.

Results and discussion

Synthesis

Previous syntheses of alkali metal-alkaline earth metal borates were performed under harsh conditions of either high temperature ($> 800\text{ }^{\circ}\text{C}$) or high pressure ($> 100\text{ bar}$) (e.g. $\text{Li}_4\text{Sr}(\text{BO}_3)_2$, $\text{NaCa}_4\text{B}_3\text{O}_9$, NaCaBO_3 , NaSrBO_3 and $\text{Li}_4\text{CaB}_2\text{O}_6$).¹⁹ A variety of acentric SHG-active alkali metal- and alkaline-earth metal borates have been prepared, which exhibited good properties including chemical and physical stabilities, wide transparency ranges and high damage thresholds. Thus, alkali metals and alkaline earth metals were used in the present study. In contrast to the aforementioned alkali metal- and alkaline-earth metal borates that were prepared under forcing conditions, we adopted a much milder hydrothermal method using $\text{Ba}(\text{NO}_3)_2$, $\text{Li}_2\text{B}_4\text{O}_7$ and KF as the starting materials and reaction at $210\text{ }^{\circ}\text{C}$. This synthetic procedure afforded a deep-UV SHG-active alkali metal-alkaline earth borate, $\text{LiBa}_3(\text{OH})(\text{B}_9\text{O}_{16})[\text{B}(\text{OH})_4]$ (**1**). In the synthesis, the excess of $\text{Li}_2\text{B}_4\text{O}_7$ is important. Firstly, it acts as a buffering material to maintain the pH of the solution, and secondly, the high ion concentrations can lead to supersaturated solutions of borate double salts. The target material was also obtained from the reaction of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, $\text{Li}_2\text{B}_4\text{O}_7$, NH_4NO_3 and KF at $210\text{ }^{\circ}\text{C}$ with a solution at the same initial pH value as the above reaction, indicating that pH plays a key role in the synthesis of borate double salts when using this convenient hydrothermal route.²⁷

Crystal Structure

Single-crystal X-ray diffraction analysis revealed that the alkali metal-alkaline earth metal borate crystal **1** crystallizes in the trigonal crystal system with polar space group $P31c$ (No. 159). In the metal borate crystal, the primary building unit (PBU), the polyborate anion $[\text{B}_9\text{O}_{19}(\text{OH})]^{12-}$, is composed of three BO_3 triangles (Δ) and six BO_4 tetrahedra (T) linked via corner- and edge-sharing modes (Fig. 1a and Scheme S1, ESI†). According to the definition proposed by Christ et al.,²⁸ the shorthand notation for the $[\text{B}_9\text{O}_{19}(\text{OH})]^{12-}$ cluster is $[9:(3\Delta+6\text{T})]$. Each $[\text{B}_9\text{O}_{19}(\text{OH})]^{12-}$ PBU is attached to six adjacent PBUs via B(2)–O(7)–B(4) linkages (Fig. 1b). Further connectivity of the $[\text{B}_9\text{O}_{19}(\text{OH})]^{12-}$ PBUs, namely through their vertices, yields a 3D framework in the ab plane with 6-membered-ring channels (Fig. 2b) in which the $[\text{B}(\text{OH})_4]^-$ anions are located (Figs. 1c and 2a). In other words, defining the $[\text{B}_9\text{O}_{19}(\text{OH})]^{12-}$ PBU as a six-connected node and the O(7) atom of the anion as a connector, the anionic framework can be regarded as possessing *pcu* topology with the Schläfli symbol $\{4^9 \cdot 6^6\}$ (Fig. 1d). This type of zeolite-like anion framework differs from some other zeolite-like compounds such as $\text{LiBa}[\text{B}_9\text{O}_{15}]$ and $\text{NaB}_3\text{O}_5 \cdot 0.5\text{H}_2\text{O}$.²⁹ In contrast to **1**, $\text{LiBa}[\text{B}_9\text{O}_{15}]$ and $\text{NaB}_3\text{O}_5 \cdot 0.5\text{H}_2\text{O}$ are both composed of $[\text{B}_3\text{O}_7]^{5-}$ PBUs, and the 3D anion frameworks of $\text{LiBa}[\text{B}_9\text{O}_{15}]$ and $\text{NaB}_3\text{O}_5 \cdot 0.5\text{H}_2\text{O}$ adopt 12-membered-ring channels and 15-membered-ring channels, respectively.

In each asymmetric unit of **1**, there is one Li atom, one Ba atom, four B atoms, and nine O atoms (Fig. 3). All atoms are located in general positions except O1, O5 and Li1 which are located on three-fold axes. B(1), B(2), and B(3) are tetrahedrally coordinated, whereas B(4) adopts a triangular BO_3 geometry. The B–O bond distances of the BO_3 and BO_4 groups are in the ranges $1.367(7)$ – $1.389(7)\text{ \AA}$ and $1.377(8)$ – $1.528(15)\text{ \AA}$, respectively. The O–B–O angles fall in the ranges $116.9(5)^{\circ}$ – $122.0(5)^{\circ}$ for the BO_3 triangles and $106.5(4)^{\circ}$ – $119.57(15)^{\circ}$ for the BO_4 tetrahedrons. These values are comparable to those of previously reported borate compounds.³⁰ In the anionic structure of **1**, $[\text{B}(4)\text{O}_3]^{3-}$ groups is almost parallel to the *c*-axis (Fig. S2, ESI†), which should be

Fig. 1 (a) $[\text{B}_9\text{O}_{19}(\text{OH})]^{12-}$ cluster unit, (b) polyhedral linking mode of $[\text{B}_9\text{O}_{19}(\text{OH})]^{12-}$ PBU and six adjacent PBUs in $\text{LiBa}_3(\text{OH})(\text{B}_9\text{O}_{16})[\text{B}(\text{OH})_4]$, (c) structure view of $\text{LiBa}_3(\text{OH})(\text{B}_9\text{O}_{16})[\text{B}(\text{OH})_4]$ with 6-membered-ring channels down the *c* axis, and (d) topological view of a 3D new 6-nodal net with the Schläfli symbol $\{4^9 \cdot 6^6\}$; the purple balls represent the six-connected nodes. Hydrogen atoms have been omitted for clarity. Symmetry code: (A) $1 - y, x - y, z$; (B) $1 - x + y, 1 - x, z$; (C) $y, x, -0.5 + z$; (D) $1 - x, -x + y, -0.5 + z$; (E) $1 + x - y, 1 - y, -0.5 + z$.

Fig. 2 (a) Perspective view of the 3D stacking structure of $\text{LiBa}_3(\text{OH})(\text{B}_9\text{O}_{16})[\text{B}(\text{OH})_4]$ with 6-membered-ring channels, and (b) view of the 6-membered-ring channels in $\text{LiBa}_3(\text{OH})(\text{B}_9\text{O}_{16})[\text{B}(\text{OH})_4]$.

Fig. 3 Asymmetric unit of $\text{LiBa}_3(\text{OH})(\text{B}_9\text{O}_{16})[\text{B}(\text{OH})_4]$. Symmetry code: (A) $-y, x-y, z$; (B) $-x, -x+y, 0.5+z$.

beneficial for enhancing NLO susceptibilities, and indeed close to a maximum possible contribution to the macroscopic SHG effect.

The Li atoms are located between two adjacent $[\text{B}_9\text{O}_{19}(\text{OH})]^{12-}$ clusters, while the Ba atoms are encapsulated in the 6-membered-ring channels (Figs. 2a and S3, ESI†). Atom Li(1) in **1** is 7-coordinate while the Ba(1) atom is 11-coordinate (Fig. S4a, ESI†). The Li–O bond distances range from 1.81 to 2.595 Å, and the Ba–O bond distances are in the range 2.677–3.103(11) Å. Bond valence sum (BVS) calculations for atoms Li(1), Ba(1), B(1), B(2), B(3) and B(4) gave values of 0.91, 2.08, 3.05, 3.04, 3.11 and 2.95, respectively, consistent with oxidation states of +1 for Li, +2 for Ba and +3 for B.³¹ Specific coordination environments of the Ba and Li atoms and the framework formed by the Ba–O and Li–O groups are shown in Fig. S4b (ESI†).

Powder X-ray Diffraction

The simulated and experimental PXRD patterns of **1** are shown in Fig. S5 (ESI†), indicating the phase purity of the products. Most peak positions of the simulated and experimental patterns are in good agreement with each other, and the differences in

Fig. 5 Thermogravimetric analysis of $\text{LiBa}_3(\text{OH})(\text{B}_9\text{O}_{16})[\text{B}(\text{OH})_4]$ under a N_2 atmosphere.

intensity may be due to the preferred orientation of the powder samples.

IR Measurement

The infrared spectrum for **1** is shown in Fig. S6 (ESI†). The broad absorption band around 3300 cm^{-1} confirms the presence of the OH groups. The strong absorption bands around $1250\text{--}1500\text{ cm}^{-1}$ can be assigned to asymmetric stretching vibrations of the BO_3 groups, while the bands centered at 1120 and 900 cm^{-1} are likely to be the asymmetric and symmetric vibrations of the BO_4 groups, respectively. The bending vibrations of BO_3 and BO_4 are seen in the range $500\text{--}800\text{ cm}^{-1}$, consistent with other metal borates containing the BO_3 and BO_4 groups.³²

Fig. 4 UV-Vis-NIR diffuse reflectance spectrum of $\text{LiBa}_3(\text{OH})(\text{B}_9\text{O}_{16})[\text{B}(\text{OH})_4]$.

UV-Vis-NIR Diffuse reflectance spectrum

The UV-Vis-NIR diffuse reflectance spectrum for **1** is shown in Figs. 4 and S7 (ESI†). The reflectance in the range $200\text{--}2000$

nm is above 80% and, in particular, the reflectance at 200 nm is about 90% (Fig. 4). No obvious absorption peak was observed for **1** in the range of 0.62–6.2 eV (Fig. S7, ESI†), except for a small absorption between ca. 5.08 and 5.84 eV, which is similar to previous reports.^{10,32} The hydroxyl groups have little effect on the UV cut-off edge of **1**. Other deep-UV NLO borates³³ contained hydroxyls have been reported. These results indicate that the experimental band gap value is greater than 6.20 eV or, in other words, the UV cut-off edge is at wavelengths below 200 nm, which is comparable to well-known Ba-, Li- or Na-containing deep-UV NLO materials such as Ba₃(ZnB₅O₁₀)PO₄ (180 nm),³⁴ Li₄Cs₃B₇O₁₄ (190 nm),³⁵ and LiNa₅Be₁₂B₁₂O₃₃ (170 nm);¹⁶ this suggests that the alkali metal-alkaline earth metal borate crystal **1** is a potential deep-UV NLO material.

Thermal Stability

Thermogravimetric analysis (TGA) of **1** (Fig. 5) shows that **1** is stable up to 300 °C. The weight losses of ca. 5.13% between 300 and 625 °C can be assigned to the removal of 2.5 water molecules formed by condensation of hydroxyl groups (calculated value 5.18%). Although hydroxyl groups exist in compound **1**, it is nevertheless stable up to a relatively high temperature, above which the hydroxyl groups are removed in the form of water molecules; the DTA curve of **1** is consistent with this.

SHG Properties

The noncentrosymmetric crystal structure of the alkali metal-alkaline earth metal borate **1** encouraged us to examine its SHG properties. SHG measurements were conducted using incident lasers at $\lambda = 1064$ nm and $\lambda = 532$ nm, respectively. KDP and BBO were selected as the references for visible and UV SHG measurements, respectively. The SHG intensities increase with increasing particle size before they reach maxima that are independent of particle size (Fig. 6), indicating that **1** is phase-matchable in both the visible and the ultraviolet region. It exhibits moderate SHG response efficiency (ca. 1.2 times as large as that of KDP) in the particle size range 150–200 μm with the incident laser at 1064 nm (Fig. 7a). With the incident laser at 532 nm, the SHG intensity of **1** is about 0.33 times that of BBO in the same particle size range (Fig. 7b).

According to anionic group theory,³⁶ the contribution of the BO₄ tetrahedra to the SHG response is small, so the SHG effect of **1** should mainly derive from the BO₃ units, which possess asymmetric electronic distributions. As described in the **Crystal Structure** section, the [BO₃]³⁻ groups are almost parallel to the *c*-axis in compound **1**. The densities of the [BO₃]³⁻ groups are 0.0076 per unit volume, which is similar to that of KBe₂BO₃F₂ (KBBF) (0.00946 per unit volume). The nonlinearity value of **1** is therefore calculated to be similar to that of KBBF (ca. $0.80 \times \text{KBBF}$),¹² while the experimental value is ~ 1.07 times that of KBBF, in good agreement.

Theoretical Studies

Fig. 6 Phase-matching curves of LiBa₃(OH)(B₉O₁₆)[B(OH)₄] with 1064 nm (a) and 532 nm (b) laser radiation.

Fig. 7 (a) Oscilloscope traces of the SHG signals for powders of LiBa₃(OH)(B₉O₁₆)[B(OH)₄] (150–200 μm) with 1064 nm (a) and 532 nm (b) laser radiation. KDP and BBO were used as references for the SHG measurements at 1064 and 532 nm, respectively.

Fig. 8 Electron density map of the valence band maximal (VBM, (a)) and conduction band minimal (CBM, (b)) for $\text{LiBa}_3(\text{OH})(\text{B}_9\text{O}_{16})[\text{B}(\text{OH})_4]$. The isosurface value is set to $0.001 \text{ eV}/\text{\AA}^3$. red: oxygen; pink: boron; green: barium; purple: lithium; gold: sodium; gray: hydrogen.

Fig. 9 Density of states (DOS) of $\text{LiBa}_3(\text{OH})(\text{B}_9\text{O}_{16})[\text{B}(\text{OH})_4]$.

To further investigate the bonding interactions in **1**, the band structure, density of states (DOS) and the electron density were calculated by density functional theory (DFT) calculations. The band structure of **1** is plotted in Fig. S8 (ESI†). From the band structure, the minimum optical band gap is 3.95 eV, in reasonable agreement with experimental results. The band gap value is smaller than the experimental value, which can be attributed to underestimation of the GGA calculations. The valence band maximal (VBM) and conduction band minimal (CBM) can be used to suggest the direct band gap for the semiconductor. To better understand the VBM and CBM, the electron densities of VBM and CBM at Γ for **1** are shown in

Fig. 8. The VBM is composed of O-2p states localized in the $[\text{B}(\text{OH})_4]^-$ unit, while the CBM is more delocalized, and mainly consists of states from the $\text{LiBa}_3(\text{OH})(\text{B}_9\text{O}_{16})^+$ unit, inducing a significant fluctuation of the first conduction band around Γ . The contributions of atoms and their orbitals to other bands around the Fermi level can be seen from the density of states (DOS) plots in Fig. 9. Several of the high valence bands (-1 – 0 eV) are dominated by O-2p orbitals, while valence bands below -2 eV involve strong hybridization of B-2p and O-2p orbitals. The conduction bands are dominated by the mixing of B-2p, O-2p and Ba-5d states. This indicates that the optical properties of **1** come primarily from the BO_3 groups.

The refractive indices dispersion curves show $n^o > n^e$ in the range 0 – 2 eV, indicating that **1** is a negative uniaxial crystal (Fig. S9, ESI†). The birefringence value of **1** at 1064 nm is somewhat small, but still satisfies the phase-matching requirement for the SHG output in the UV and visible spectral regions.³⁷ According to the Kleinman rule, the space group (159, class 3m) of **1** has 8 non-vanishing SHG tensors, which include the $d_{11} = -d_{12} = -d_{26}$, $d_{15} = d_{25}$, $d_{31} = d_{32}$, and d_{33} components. Therefore, only 4 independent SHG tensors remain, namely, d_{11} , d_{15} , d_{31} and d_{33} . The SHG coefficients of d_{11} , d_{15} , d_{31} and d_{33} at 1064 nm (1.165 eV) are 0.63×10^{-9} , 0.55×10^{-9} , 0.84×10^{-9} and 2.63×10^{-9} esu, respectively. The highest value of a tensor component of compound **1** is 2.63×10^{-9} esu, slightly larger than the experimental value ($1.2 \times \text{KDP}$ for **1**). This is not surprising, because the SHG calculations are based on single crystals that generate larger SHG effects.³⁸

Conclusions

In summary, a new NCS alkali metal-alkaline earth metal borate, $\text{LiBa}_3(\text{OH})(\text{B}_9\text{O}_{16})[\text{B}(\text{OH})_4]$, has been prepared by a convenient hydrothermal method. The structure consists of $[\text{B}_9\text{O}_{19}(\text{OH})]^{12-}$ PBUs and features a 3D anionic framework. The compound exhibits a moderate SHG response (ca. $1.2 \times \text{KDP}$) and short UV cutoff edges (below 200 nm), and is phase-matchable not only in the visible region, but also in the ultraviolet region. These features make $\text{LiBa}_3(\text{OH})(\text{B}_9\text{O}_{16})[\text{B}(\text{OH})_4]$ a potential deep-UV NLO material. Further research on the deep-UV SHG-active alkali metal-alkaline earth metal borate system is currently in progress.

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