

Electronic Supplementary Information

Design of Deep-Ultraviolet Nonlinear Optical Materials Based on Fundamental Building Blocks with Excellent Microscopic Properties

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Calculations Details

The electronic and band structures as well as linear optical property calculations were performed by employing CASTEP,¹ a plane-wave pseudopotential DFT package, with the norm-conserving pseudopotentials (NCP).² The exchange-correlation functional was Perdew-Burke-Emzerhoff (PBE) functional within the generalized gradient approximation (GGA).³⁻⁵ The plane-wave energy cutoff was set at 950.0 eV. Self-consistent field (SCF) calculations were performed with a convergence criterion of 0.5×10^{-6} eV/atom on the total energy. The k-point separation for each material was set as 0.05 \AA^{-1} in the Brillouin zone,⁶ resulting in corresponding Monkhorst-Pack k-point meshes. The empty bands are set as 3 times of valence bands in the calculation to ensure the convergence of SHG coefficients. For other calculation parameters and convergence criteria, we retained the default values and used the linear response method to calculate phonon dispersion.

The calculations of the linear optical performance were described in terms of the complex dielectric constant $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$. The imaginary part $\epsilon_2(\omega)$ of the dielectric function $\epsilon(\omega)$ was calculated by using momentum matrix elements between the occupied and unoccupied electronic states:

$$\epsilon_2(\hbar\omega) = \frac{2e^2\pi}{\Omega\epsilon_0} \sum_{kcv} \left| \langle \psi_k^c | \hat{u} \cdot r | \psi_k^v \rangle \right|^2 \delta[E_k^c - E_k^v - E]$$

Here Ω is the unit cell volume, v and c represent the valence band (VB) and conduction band (CB), respectively. ω and \hat{u} are the frequency and the unit vector in the polarization direction of the incident light. Under the periodic boundary condition, $\left| \langle \psi_k^c | \hat{u} \cdot r | \psi_k^v \rangle \right|$ is the transition matrix element between the VB and the CB at a specific k point in the first Brillouin zone. The real part $\epsilon_1(\omega)$ can be obtained from the imaginary part $\epsilon_2(\omega)$ using the Kramers–Kronig transformation. The refractive indices n and birefringence Δn can be obtained from the complex dielectric function.

The SHG coefficients were calculated using the so-called length-gauge formalism derived by Aversa and Sipe.⁷ At zero frequency, the static second-order NLO susceptibilities can be ascribed to the virtual hole (VH) and virtual electron (VE) processes:⁸

$$\chi_{\alpha\beta\gamma}^{(2)} = \chi_{\alpha\beta\gamma}^{(2)}(\text{VE}) + \chi_{\alpha\beta\gamma}^{(2)}(\text{VH})$$

Where $\chi_{\alpha\beta\gamma}^{(2)}(\text{VE})$ and $\chi_{\alpha\beta\gamma}^{(2)}(\text{VH})$ are computed using the following formulas:

$$\chi_{\alpha\beta\gamma}^{(2)}(\text{VE}) = \frac{e^3}{2\hbar^2 m^3} \sum_{vcc'} \int \frac{d^3k}{4\pi^3} P(\alpha\beta\gamma) \text{Im}[p_{cv}^\alpha p_{cc'}^\beta p_{c'v}^\gamma] \times \left(\frac{1}{\omega_{cv}^3 \omega_{v'c'}^2} + \frac{2}{\omega_{vc}^4 \omega} \right)$$

$$\chi_{\alpha\beta\gamma}^{(2)}(\text{VH}) = \frac{e^3}{2\hbar^2 m^3} \sum_{v'c} \int \frac{d^3k}{4\pi^3} P(\alpha\beta\gamma) \text{Im}[p_{v'v}^\alpha p_{v'c}^\beta p_{cv}^\gamma] \times \left(\frac{1}{\omega_{cv}^3 \omega_{v'c}^2} + \frac{2}{\omega_{vc}^4 \omega} \right)$$

Here, α , β , and γ are the Cartesian components; v/v' and c/c' denote the VBs and CBs; $P(\alpha\beta\gamma)$, $\hbar\omega_{ij}$, and p_{ij}^α refer to the full permutation, band energy difference, and momentum matrix elements, respectively.

To balance the calculation efficiency and accuracy of the optical properties under a high-density k-mesh, the GGA and scissors-corrected methods were adopted. The scissors operator was set as the difference between the calculated HSE06 and GGA bandgap. The HSE06 hybrid functional was employed to calculate more accurate bandgap value using the PWmat code,⁹ which were shown to be consistent with experimental results. The polarizability anisotropy ($\Delta\alpha$) and hyperpolarizability ($|\beta_{\max}|$) of $[\text{B}_3\text{O}_7]$, $[\text{B}_3\text{O}_6\text{F}]$ and $[\text{B}_3\text{O}_6\text{F} + \text{BO}_3]$ anionic groups in molecular level are calculated using the DFT method implemented by the Gaussian09 package.

In fact, the structure of $\text{Li}_2\text{B}_3\text{O}_5\text{F}$ is built based on the known structure $\text{Li}_2\text{B}_3\text{O}_4\text{F}_3$. In $\text{Li}_2\text{B}_3\text{O}_4\text{F}_3$, the B (1) O_3 group and B (2) O_3F group in $[\text{B}_3\text{O}_5\text{F}_3]$ form a one-dimensional $[\text{B}_3\text{O}_5\text{F}_3]_\infty$ chain on the b - c plane by sharing O atoms, and the Li atoms are located between the two chains. The one $[\text{BO}_3]$ triangle, one $[\text{BO}_3\text{F}]$ tetrahedra and one $[\text{BO}_2\text{F}_2]$

tetrahedra are linked through the sharing oxygen atom to form a $[B_3O_5F_3]$ ring, this is the basic building block of $Li_2B_3O_4F_3$. In $Li_2B_3O_5F$, the B (1) O_3 group and B (2) O_3F group in $[B_3O_5F]$ form a one-dimensional $[B_3O_6F]_\infty$ chain on the $b-c$ plane by sharing O atoms, and the Li atoms are located between the two chains. The two $[BO_3]$ triangles and one $[BO_3F]$ tetrahedra are linked through the sharing oxygen atom to form a $[B_3O_6F]$ ring, this is the basic building block of $Li_2B_3O_5F$. The structure of $Li_2B_3O_5F$ is similar to that of the known crystal $Li_2B_3O_4F_3$, both of which are crystallized in the $P2_12_12_1$ space group, but with a different FBB. Substitute $[BO_2F_2]$ group in $[B_3O_5F_3]$ group with $[BO_3]$ group to form $[B_3O_6F]$ group, thus forming $Li_2B_3O_5F$ from the known structure $Li_2B_3O_4F_3$.

Table S1. The crystallographic data of $\text{Li}_2\text{B}_3\text{O}_5\text{F}$, including cell parameters, fractional coordinates, bond lengths and bond valence sum (BVS).

$\text{Li}_2\text{B}_3\text{O}_5\text{F}$					
$P2_12_12_1$ (19)					
Cell parameters					
a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
4.750	8.790	12.820	90	90	90
Fractional coordinates					
Atoms	x	y	z		
Li1	0.6739	0.6696	0.3799		
Li2	1.5955	0.1365	0.5908		
B1	1.0817	0.3012	0.6678		
B2	0.9946	0.5205	0.5485		
B3	1.0329	0.5594	0.7368		
O1	1.0150	0.3645	0.5672		
O2	1.0348	0.6183	0.6364		
O3	1.0131	0.4066	0.7533		
O4	1.0564	0.6537	0.8211		
O5	0.9550	0.5703	0.4530		
F1	1.3837	0.2730	0.6743		
Bond lengths (Å)					
Li1-O2	1.989	Li1-O3	1.969		
Li1-O5	1.850	Li2-O1	2.062		
Li2-O4	2.007	Li2-O5	2.018		
Li2-F1	1.897	B1-O1	1.440		
B1-O3	1.472	B1-O4	1.461		
B1-F1	1.458	B2-O1	1.396		
B2-O2	1.420	B2-O5	1.314		
B3-O2	1.388	B3-O3	1.363		

B3-O4		1.366			
BVS					
Li1	0.86	Li2	0.89	B1	2.99
B2	2.96	B3	2.99	O1	1.97
O2	2.05	O3	2.04	O4	2.03
O5	1.75	F1	0.90		

Table S2 The calculated band gaps, birefringence and d_{ij} of β -BaB₂O₄, LiB₃O₅, NH₄B₄O₆F, CsB₄O₆F and KH₂PO₄ are compared with the experimental values.

Compounds	Space group	Band gap (eV)	Birefringence at 1064 nm	SHG coefficient (pm/V)	Cutoff edge (nm)	Shortest λ_{PM} (nm)
β -BaB ₂ O ₄ ¹⁰	<i>R3c</i>	6.56	0.1	$d_{22} = \pm 2.3$	189	205
β -BaB ₂ O ₄ *	<i>R3c</i>	6.43	0.106	$d_{22} = \pm 2.0$	193	209
LiB ₃ O ₅ ^{10,11}	<i>Pna2₁</i>	7.98	0.040	$d_{31} = 0.67$ $d_{32} = 0.85$ $d_{33} = 0.04$	156	276
LiB ₃ O ₅ *	<i>Pna2₁</i>	8.20	0.046	$d_{31} = 0.72$ $d_{32} = 0.80$ $d_{33} = 0.05$	152	269
NH ₄ B ₄ O ₆ F ¹²	<i>Pna2₁</i>	7.95	0.119	1.17	156	158
NH ₄ B ₄ O ₆ F*	<i>Pna2₁</i>	7.70	0.107	$d_{31} = 0.02$ $d_{32} = 1.10$ $d_{33} = -1.25$	161	169
CsB ₄ O ₆ F ¹³	<i>Pna2₁</i>	8.00	0.114	0.741	155	172
CsB ₄ O ₆ F*	<i>Pna2₁</i>	7.91	0.098	$d_{15} = -0.07$ $d_{32} = 0.95$ $d_{33} = -0.95$	157	177
KH ₂ PO ₄ ^{10,14}	$\bar{I}4\ 2d$	7.26	0.034	$d_{36} = 0.39$	171	240
KH ₂ PO ₄ *	$\bar{I}4\ 2d$	7.31	0.044	$d_{36} = 0.35$	170	233

* This work;

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