Electronic Supplementary Information for

An outstanding Second-Harmonic Generation Material BiB_2O_4F: Exploiting the Electron-withdrawing Ability of Fluorine

Rihong Cong,[a] Ying Wang,[a] Lei Kang,[b,c] Zhengyang Zhou,[a] Zheshuai Lin,[b*] Tao Yang,[a*]*

[a] College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, People's Republic of China

[b] Beijing Center for Crystal R&D, Key Lab of Functional Crystals and Laser Technology, Technical Institute of Physics and Chemistry, Chinese Academy of Science, P.O. Box 2711, Beijing 100080, People's Republic of China

[c] University of Chinese Academy of Sciences, Beijing 100049, PR China

*Correspondence authors, email: congrihong@cqu.edu.cn, zslin@mail.ipc.ac.cn and taoyang@cqu.edu.cn; Tel: (86 23)65105065; Fax: (86 23)65105065.

Computational method

The electronic structure and SHG coefficients for BiB_2O_4F and $BiB_2O_4(OH)$ were calculated using the first-principles plane-wave pseudopotential method implemented in the CASTEP program.[1,2] The local density approximation (LDA) is adopted to describe the exchange-correlation (XC) functionals.[3] The ion-electron interactions are modeled by the optimized norm-conserving pseudopotentials of the Kleinman-Bylander form for all constituent elements.[4,5] In this model, Bi $5d^{10}6s^26p^3$, B $2s^22p^1$, O $2s^22p^4$, and F $2s^22p^5$ electrons are treated as the valence electrons, respectively. A kinetic energy cutoff of 900 eV and Monkhorst-Pack *k*-point meshes[6] spanning less than 0.04/Å^3 in the Brillouin zone were chosen to ensure the present purposes to be sufficiently accurate. It is known that the position of hydrogen atoms cannot be determined accurately by experiments, but these approximate locations provide the initial structures for the further theoretical optimization. The geometries are optimized by the Broyden, Fletcher, Goldfarb, and Shannon minimizer.[7] The convergence thresholds between optimization cycles for energy change, maximum force, maximum stress, and maximum displacement are set as 5×10^{-5} eV/atom, 0.01 eV/Å, 0.02 GPa, and 0.0005 Å, respectively. The optimization terminates when all of these criteria are satisfied.

Based on the calculated electronic structures, the linear optical refractive indices and the SHG coefficients of BiB_2O_4F and $BiB_2O_4(OH)$ were determined. The refractive indices were calculated through the Kromer-Kronig transformation from the

imaginary part of the dielectric function, which can be obtained with the matrix elements that describe the electronic transitions between the ground and excited states in the crystal considered. Since the energy band gap of BiB_2O_4F and $BiB_2O_4(OH)$ are much larger than the frequency of incident light (i.e. at the wavelength of 1064 nm), the dispersion of the SHG effects is neglectable, so the static limit of SHG coefficients is accurate enough to characterize their non-resonant NLO properties. The static SHG coefficients were calculated by the formula developed by Lin et al.,[8, 9] and further the microscopic structural origins are investigated by the real-space atom-cutting technique.[9] The same computational and analysis methodology has been implemented in the CASTEP academic code and successfully applied on various NLO crystals, such as LBO-family,[10] KDP[11] and BIBO.[12] It is well known that the band-gap calculated by LDA is usually smaller than the experimental data due to the discontinuity of exchange-correlation energy. Thus, a scissors operator is used to shift upward all the conduction bands (CB) in order to agree with measured values of the band-gap.[13]

Reference

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Table S1. X-ray data collection conditions, crystallographic and structure refinement parameters for $BiB_2O_4(OH)$.

Chemical formula	$BiB_2O_4(OH)$
Deposition number	CCDC1014612
Space group (number)	$P3_1$ (144)
Lattice parameters (Å)	a = 6.62214(10), c = 6.65264(10)
V (Å^3)	252.652(8)
Z	3
D_x (g·cm^{-3})	6.144
Radiation type, λ (Å)	Mo $K\alpha_1$, 0.71073
Specimen form, color and size (mm)	Block, colorless, 0.05 × 0.05 × 0.05
Diffractometer	SuperNova equipped with Eos
Temperature (K)	104
F_{000}	402
μ(Mo K$_\alpha$) (mm^{-1})	52.218
θ range (deg)	3.553-28.995
Number of reflections	448
Number of refined parameters	35
Number of restraints	1
Structure determination	Direct method
Structure refinement	Shelx97
R_{int}	0.0276
Final R indices [I > 2σ(I)]	R_1 = 0.0418
	wR_2 = 0.0915
R indices (all data)	R_1 = 0.0443
	wR_2 = 0.0934

GOF	1.018

Table S2. Fractional atomic coordinates, isotropic thermal displacement factors and BVS (Bond Valence Sum) values for $BiB_2O_4(OH)$.

Atom	*x*	*y*	*z*	U_{eq} /Å^2	BVS
Bi	0.4654(2)	1.0395(2)	-0.5020(8)	0.0018(3)	2.87
O1	0.652(4)	0.811(4)	-0.472(4)	0.004(3)	2.09
O2	0.342(4)	0.148(4)	-0.895(3)	0.004(3)	2.13
O3	0.589(4)	1.433(4)	-0.529(3)	0.004(3)	2.03
O4	1.076(4)	1.038(4)	-0.389(3)	0.004(3)	1.58
O5	0.384(4)	0.490(4)	-0.260(3)	0.000(5)	0.98
B1	0.882(9)	0.989(9)	-0.531(7)	0.022(11)	2.95
B2	0.609(7)	0.603(6)	-0.363(5)	0.001(7)	2.99
H	0.2045	0.6152	0.5183		

Table S3. Selected bond distances (Å) for $BiB_2O_4(OH)$.

Atom-atom	bond lengths (Å)	Atom-atom	bond lengths (Å)
Bi–O1	2.39(2)	B1-O1	1.44(6)
Bi–O2	2.27(2)	B1-O2	1.48(6)
Bi–O3	2.31(2)	B1-O4	1.50(6)
Bi–O3	2.16(2)	B1-O4	1.52(5)
Bi–O4	2.68(2)	B2-O1	1.45(4)
Bi–O5	2.69(2)	B2-O2	1.47(4)
		B2-O3	1.54(4)

		B2-O5	1.46(4)

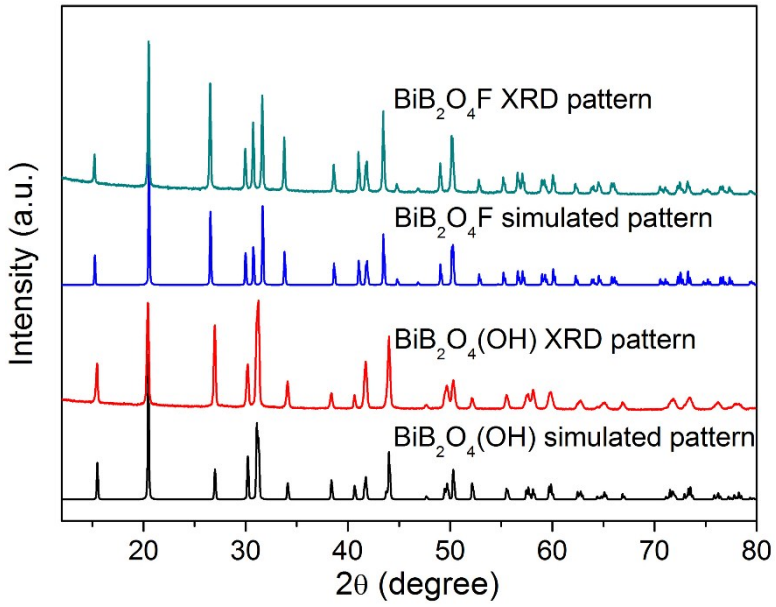

Fig. S1. Typical powder XRD patterns for $BiB_2O_4(OH)$ and BiB_2O_4F, where the simulated patterns based on their crystal structures are also presented for comparison.

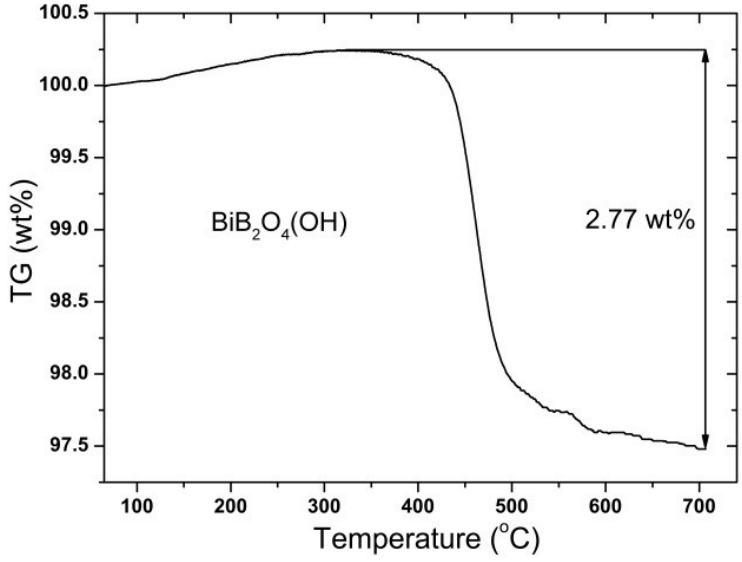

Fig. S2. TG curve of as-synthesized $BiB_2O_4(OH)$.

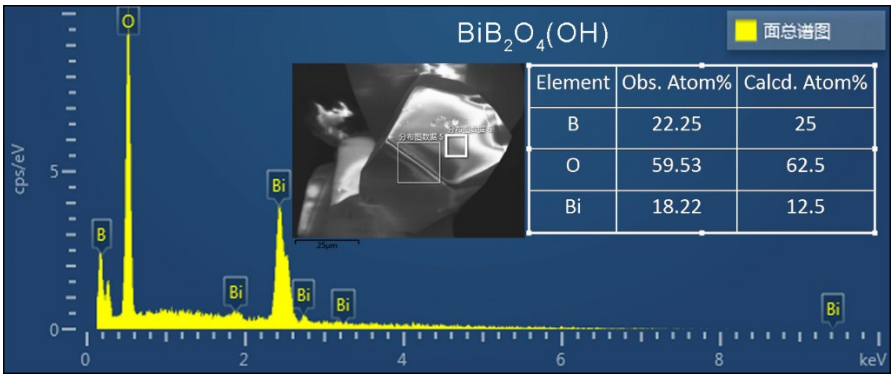

Fig. S3. SEM and EDX on a selected $BiB_2O_4(OH)$ crystal. The observed atomic ratio is close to the expected formula, expect that the Bi content is slightly high. Considering the large experimental error for SEM/EDX on heavy atoms, this deviation is acceptable. In fact, in the previous report (L. Y. Li, G. B. Li, Y. X. Wang, F. H. Liao, J. H. Lin, Chem. Mater., 2005, 17, 4174-4180), the authors has performed an elemental analysis by inductively coupled plasma-atomic emission spectrometry (ICP-AES) on both BiB_2O_4F and $BiB_2O_4(OH)$, where the obtained B:Bi mole ratios were 1.93 and 2.06, respectively.