Supporting Information

Alkali metal-alkaline earth metal borate crystal $LiBa_3(OH)(B_9O_{16})[B(OH)_4]$ as a new deep-UV nonlinear optical material†

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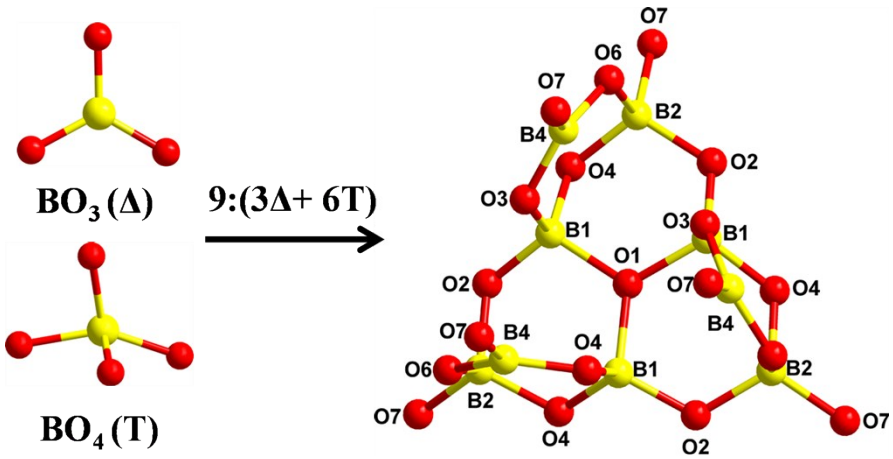
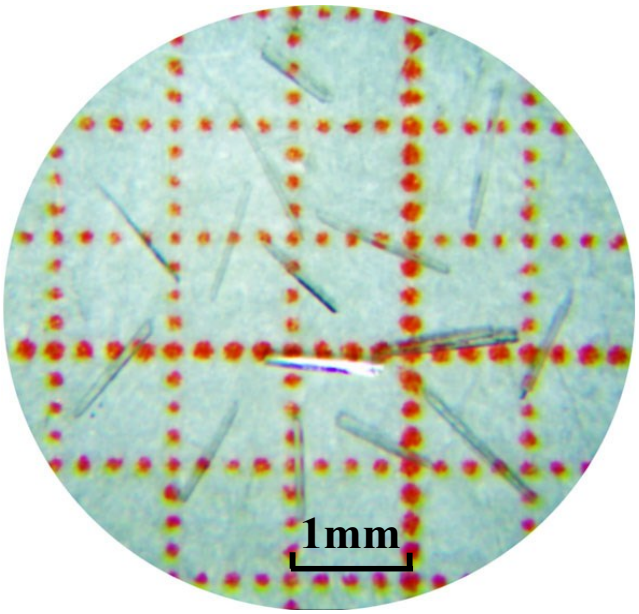
Table S1. Selected bond distances (Å) and angles (deg) for $LiBa_3(OH)(B_9O_{16})[B(OH)_4]$[a].

B(1)-O(4)	1.432(7)	B(1)-O(2)	1.434(7)
B(1)-O(3)	1.511(7)	B(1)-O(1)	1.519(6)
B(2)-O(4)#1	1.448(7)	B(2)-O(2)	1.466(7)
B(2)-O(7)	1.474(7)	B(2)-O(6)	1.506(7)
B(3)-O(8)#2	1.377(8)	B(3)-O(8)	1.377(8)
B(3)-O(8)#3	1.377(8)	B(3)-O(9)	1.528(15)
B(4)-O(7)#4	1.367(7)	B(4)-O(3)	1.376(7)
B(4)-O(6)#5	1.389(7)		
Ba(1)-O(2)	2.747(4)	Ba(1)-O(2) #7	2.871(3)
Ba(1)-O(3)	2.925(4)	Ba(1)-O(4) #7	2.677(4)
Ba(1)-O(5)	2.7097(11)	Ba(1)-O(6)	3.065(4)
Ba(1)-O(6) #8	2.780(4)	Ba(1)-O(7) #8	3.032(4)
Ba(1)-O(8)	3.103(11)	Ba(1)-O(8) #7	2.993(10)
Ba(1)-O(9)#7	2.852(14)		
Li(1)-O(3) #9	2.595(18)	Li(1)-O(3) #6	2.595(18)
Li(1)-O(3) #10	2.595(18)	Li(1)-O(5)	1.81(2)
Li(1)-O(7)	2.239(4)	Li(1)-O(7) #8	2.239(4)
Li(1)-O(7) #11	2.239(4)		
O(4)-B(1)-O(2)	109.9(4)	O(4)-B(1)-O(3)	109.8(4)
O(2)-B(1)-O(3)	112.0(4)	O(4)-B(1)-O(1)	108.1(4)
O(2)-B(1)-O(1)	110.0(4)	O(3)-B(1)-O(1)	106.9(4)
O(4) #1-B(2)-O(2)	111.7(4)	O(4) #1-B(2)-O(7)	111.4(4)
O(2)-B(2)-O(7)	111.2(4)	O(4) #1-B(2)-O(6)	107.9(4)
O(2)-B(2)-O(6)	107.8(4)	O(7)-B(2)-O(6)	106.5(4)
O(8)-B(3)-O(8) #2	119.57(15)	O(8)-B(3)-O(8) #3	119.57(15)
O(8) #2-B(3)-O(8) #3	119.57(15)	O(8) #2-B(3)-O(9)	118.5(9)
O(8) #3-B(3)-O(9)	98.7(9)	O(9)-B(3)-O(8)	98.7(9)
O(7) #4-B(4)-O(3)	116.9(5)	O(7) #4-B(4)-O(6) #5	122.0(5)
O(3)-B(4)-O(6) #5	121.1(5)		

[a] Symmetry codes: #1 - y+1, x-y+1, z; #2 -y, x-y, z; #3 -x+y, -x, z;
#4 x-y, -y+1, z-1/2; #5 –x+y, -x+1, z; #6 -x+1, -x+y, z+1/2;
#7 x, y, z-1/2; #8 –y+1, x-y, z; #9 x, y, z+1/2;
#10 x-y+1, -y+1, z+1/2; #11 –x+y+1, -x+1, z.

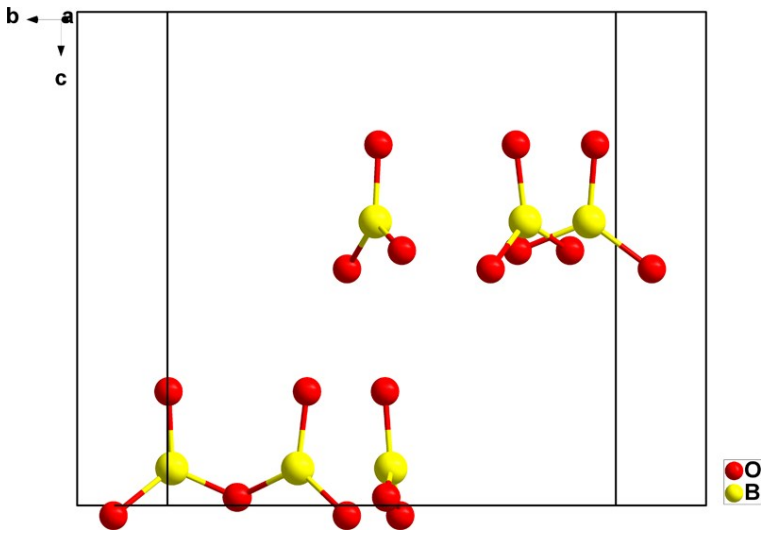


Scheme S1. $[B_9O_{19}(OH)]^{12-}$ cluster unit constructed from BO_3 and BO_4 units.



(a)

Figure S1. Photograph of $LiBa_3(OH)(B_9O_{16})[B(OH)_4]$.



(a)

Figure S2. Arrangement of $[BO_3]^{3-}$ groups of $LiBa_3(OH)(B_9O_{16})[B(OH)_4]$ along the *c*-axis.

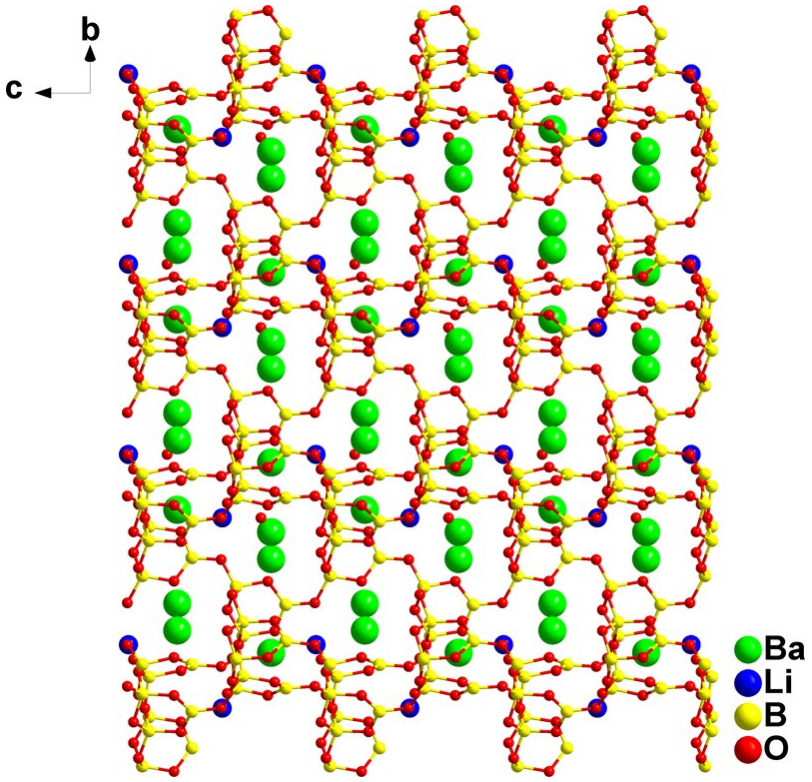
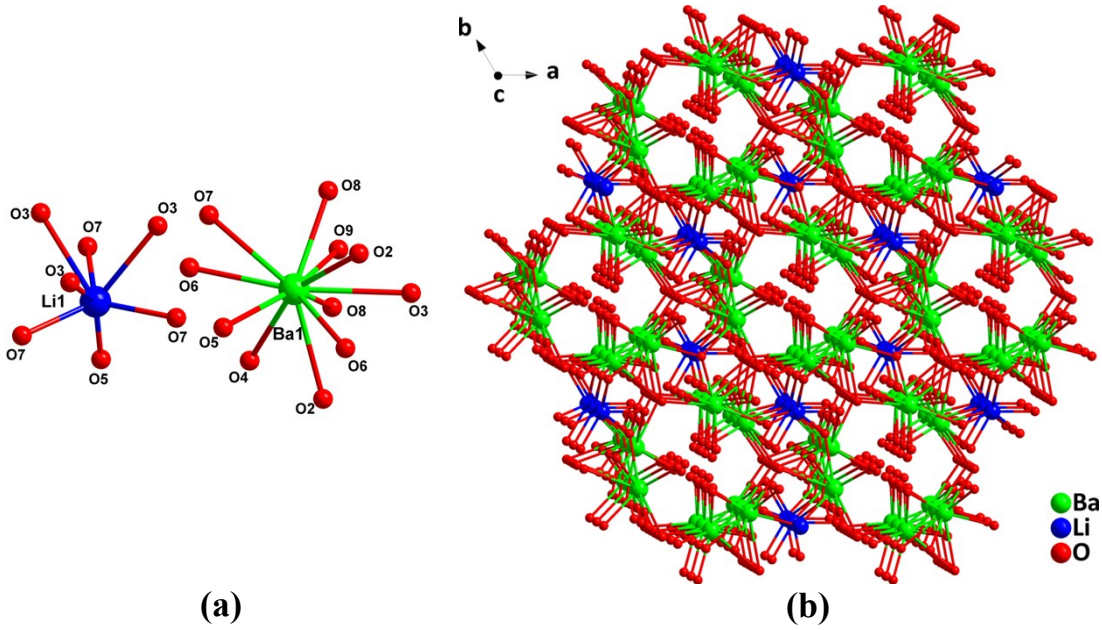


Figure S3. Structure view of $LiBa_3(OH)(B_9O_{16})[B(OH)_4]$ down the *a*-axis.



(a) **(b)**

Figure S4. Coordination environments of the Ba and Li atoms in $LiBa_3(OH)(B_9O_{16})[B(OH)_4]$ (a), and the 3D framework formed by the Li-O and Ba-O groups (b). Hydrogen atoms have been omitted for clarity.

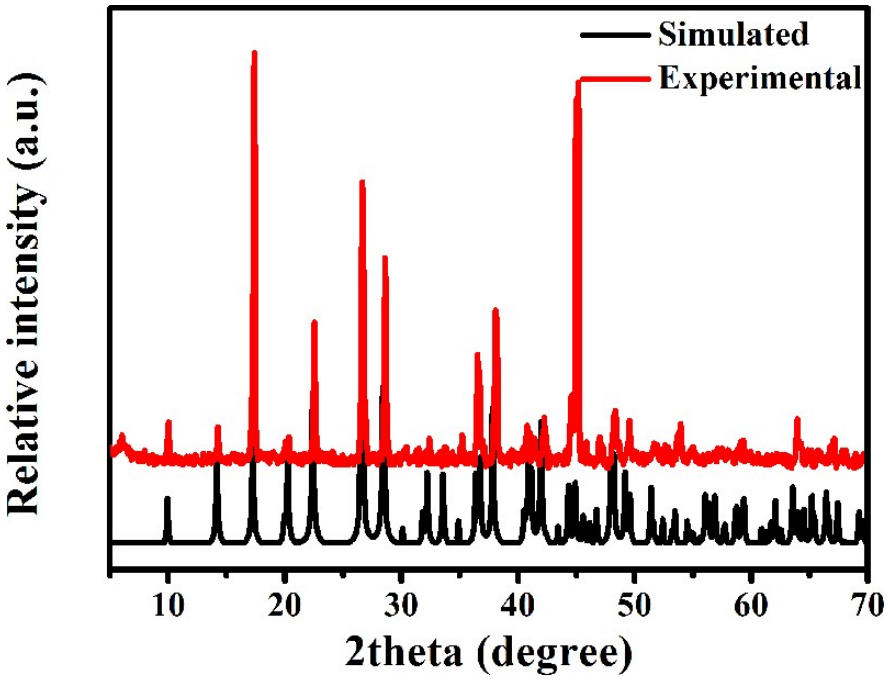


Figure S5. Experimental and simulated powder X-ray diffraction patterns of $LiBa_3(OH)(B_9O_{16})[B(OH)_4]$.

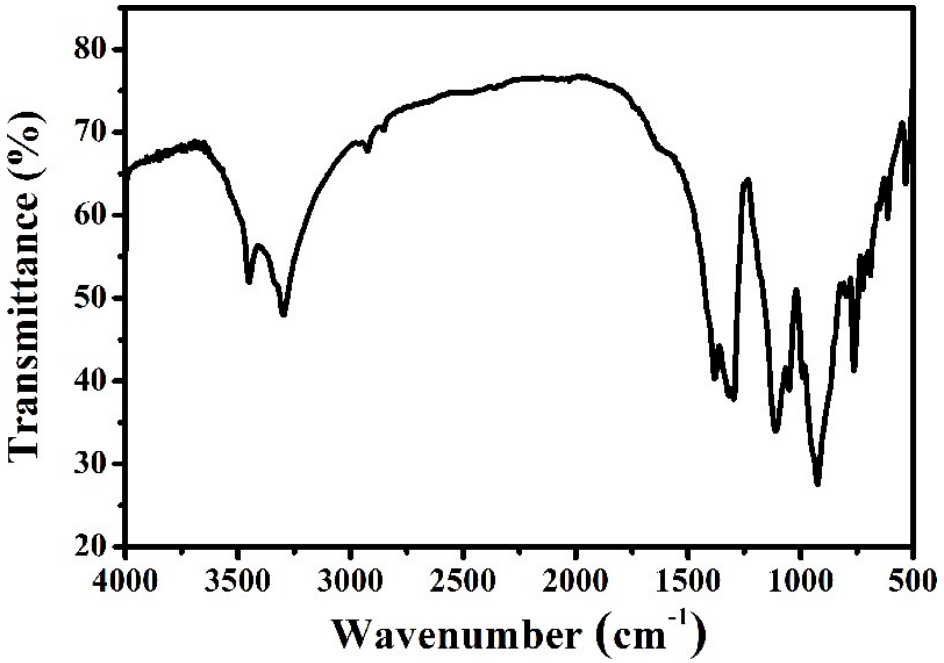


Figure S6. IR spectrum of $LiBa_3(OH)(B_9O_{16})[B(OH)_4]$.

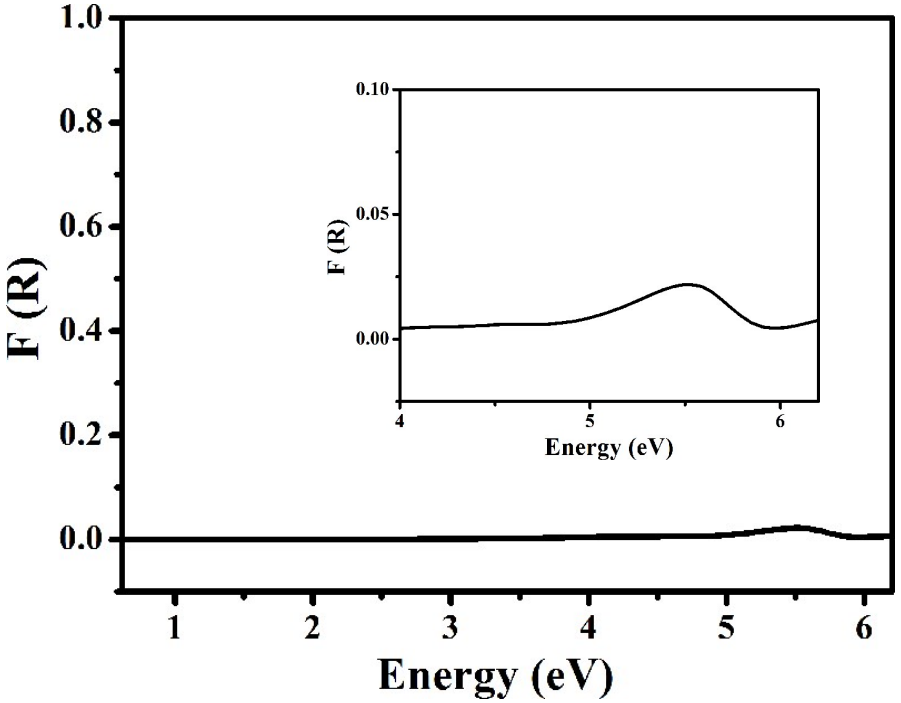


Figure S7. UV-Vis-NIR diffuse reflectance absorption spectra of $LiBa_3(OH)(B_9O_{16})[B(OH)_4]$.

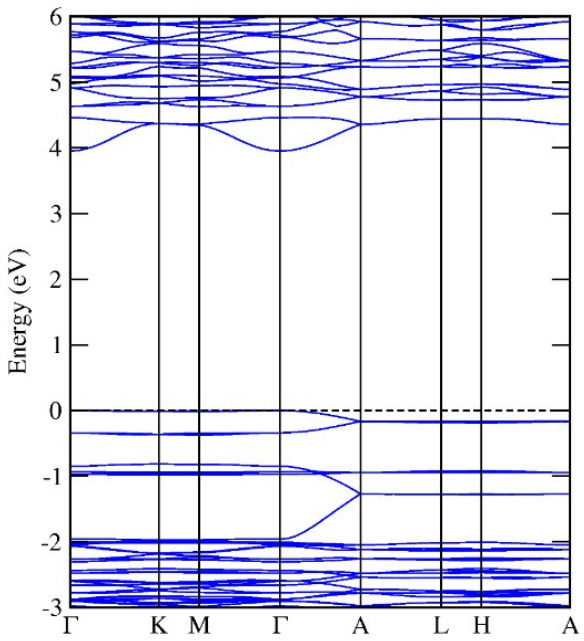


Figure S8. Band structure of $LiBa_3(OH)(B_9O_{16})[B(OH)_4]$.

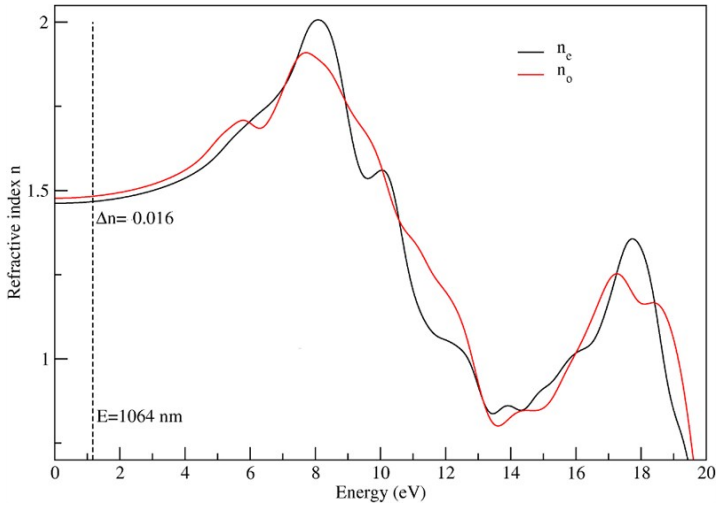


Figure S9. Calculated refractive indexes of $LiBa_3(OH)(B_9O_{16})[B(OH)_4]$.