Supporting information

Synthesis, Growth and Characterization of a Third-order Nonlinear Optical Crystal Based on the Borate Ester with Sodium Supporting its Structural Framework

Zhihua Sun,[†] Tianliang Chen,[†] Ning-ning Cai,[‡] Jing-wei Chen,[§] Lina Li,[†] Yan Wang,[†] Junhua Luo,*[,†] and Maochun Hong[†]

[†] *Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China*

[‡] *State Key Laboratory of Crystal Materials and Institute of Crystal Materials, Shandong University, Jinan 250100, China*

[§] *Department of Optics, Shandong University, Jinan 250100, China*

* To whom correspondence should be addressed. E-mail: sunzhihua@fjirsm.ac.cn.

Tel: +86-591-83730955; Fax: +86-591-83730955

Element analysis: Calculated results are H: 3.96 B: 3.04 C: 53.97 O: 32.57 Na: 6.46**;** Experimental results are H: 4.02 B: 2.97 C: 54.20 O: 32.06 Na: 6.05

NMR spectral data: ^{13}C NMR (D_2O, 298 K, TMS): 179.8, 177.9, 139.3, 137.5, 129.1, 129.0, 128.6, 127.1, 126.7, 126.6, 78.3, 78.1, 73.9;

^{1}H NMR (D_2O, 298 K, TMS): 7.47-7.37 (m, 5H), 5.45, 5.09 (m, 1H)

X-ray Crystallography

X-ray powder diffraction (XRPD) was used to characterize the grown bulk crystals. Experimental XRPD patterns have been proved to be well consistent with calculated values derived from the single-crystal data by the mercury program，which are shown in Figure S3. The detailed experimental values and indices are given in Table S2.

Tables

Table S1. Selected bond lengths [Å] and angles [deg] for LMBNa crystal.

	Bond length		Bond length		Bond length
B1-O1	1.456(3)	B1-O2	1.497(5)	B2-O10	1.441(3)
B1-O4	1.430(3)	B2-O7	1.438(5)	B2-O11	1.492(3)
B1-O5	1.498(3)	B2-O8	1.511(5)	B2-O7	1.440(3)
Na1-O3	2.309(2)	Na1-O14	2.315(4)	Na3-O1	2.515(3)
Na1-O5	2.759(3)	Na2-O1	2.370(2)	Na3-O10	2.269(3)
Na1-O6	2.3960(2)	Na2-O7	2.363(3)	Na3-O13	2.338(7)
Na1-O9	2.4376(2)	Na2-O10	2.611(3)	Na3-O14	2.222(7)
Na1-O12	2.4966(2)	Na2-O13	2.403(6)	Na3-O7	2.363(3)
Na1-O13	2.443(8)	Na2-O14	2.315(4)		
	Bond angle		Bond angle		Bond angle
O4-B1-O1	113.71(19)	O7-B2-O8	104.39(19)	O14-Na1-O13	69.86(18)
O4-B1-O2	113.98(19)	O8-B2-O10	113.98(19)	O13-Na2-O14	90.7(2)
O1-B1-O2	104.3(2)	O8-B2-O11	106.5(2)	O10-Na2-O13	101.9(2)
O4-B1-O5	105.2(2)	O3-Na1-O6	83.22(7)	O9-Na2-O14	81.69(12)
O1-B1-O5	112.94(19)	O6-Na1-O12	112.24(6)	O10-Na2-O14	79.68(12)
O2-B1-O5	106.71(13)	O12-Na1-O9	79.35(6)	O10-Na2-O15	100.79(17)
O7-B2-O10	113.7(2)	O14-Na1-O3	88.14(16)	O14-Na2-O1	168.65(16)
O11-B2-O7	113.91(18)	O12-Na1-O14	64.45(13)	O14-Na3-O1	117.8(2)
O10-B2-O11	104.41(19)	O5-Na1-O14	133.40(14)	O14-Na3-O7	126.3(2)

Table S2 The experimental *d* values (observed), 2θ (observed and calculated) and their diffraction indices for LMBNa crystal

h	k	l	$2\theta_{obs}$	$2\theta_{cal}$	d_{obs}	h	k	l	$2\theta_{obs}$	$2\theta_{cal}$	d_{obs}
0	0	2	7.448	7.448	11.8592	4	1	-4			
1	0	1		7.495		0	2	4	25.720	25.720	3.4609
1	0	-3		11.089		3	2	-2	26.666	26.666	3.3403
0	0	3	11.182	11.182	7.9061	1	1	6		16.766	
2	0	0		11.184		4	1	2	27.654	27.654	3.2232
2	0	-2	11.672	11.672	7.5759	1	2	-5		27.671	
1	1	-1	11.903	11.903	7.4294	2	2	-5		28.378	
2	0	1		12.702		3	0	5	28.452	28.452	3.1346
0	1	2	12.779	12.779	6.9218	3	2	-4		28.544	
1	1	1		12.806		5	1	-5	29.388	29.388	3.0367
1	1	-2	13.129	13.129	6.7378	5	1	-1		29.388	
0	0	4		14.929		5	1	-5		29.452	
2	1	-1	14.977	14.996	5.9104	5	1	0		29.455	
2	0	2	14.996	15.023	5.9032	3	2	-5		30.171	
1	1	-3	15.204	15.204	5.8229	1	2	-6	30.218	30.218	2.9552
0	1	3		15.273		4	2	-2		30.256	
2	1	0		15.274		1	1	7		30.261	
3	1	-1	19.284	19.284	4.5992	4	2	-1		30.304	
3	0	-4		19.305		0	2	6		30.825	
3	1	-2	19.502	19.502	4.5482	4	2	0	30.827	30.827	2.8982
3	1	0	19.790	19.790	4.4827	5	1	-5		31.302	
3	1	-3	20.422	20.422	4.3452	5	1	1	31.303	31.303	2.8553
2	1	3	20.680	20.680	4.2916	2	0	7		31.349	
0	2	1	21.161	21.161	4.1950	4	1	4	32.118	32.118	2.7846
0	0	6	22.473	22.473	3.9531	1	0	8		32.141	
4	0	0		22.476		3	1	-8		32.173	
1	2	2		23.348		3	2	-6		32.179	
1	1	5	23.401	23.401	3.7983	4	2	-5		32.888	
2	1	4		23.448		5	1	-6		32.894	
1	1	-6	24.062	24.062	3.6956	5	1	2	32.905	32.895	2.7198
4	1	-2		24.108		2	2	-7		33.285	
2	2	1	24.467	24.467	3.6353	6	0	-4		33.296	
1	0	-7	25.351	25.351	3.5105	2	3	-1	33.353	33.353	2.6843
2	0	-7		25.674		3	1	6		33.424	

Figures

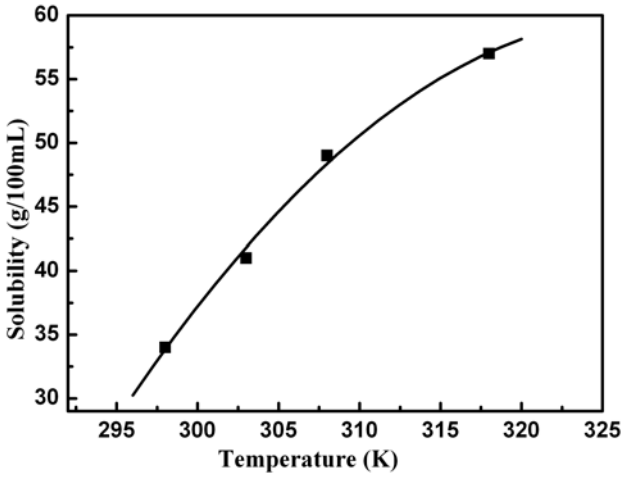

Figure S1. Solubility curve of LMBNa crystal in water

Figure S2. The grown LMBNa crystal with high quality.

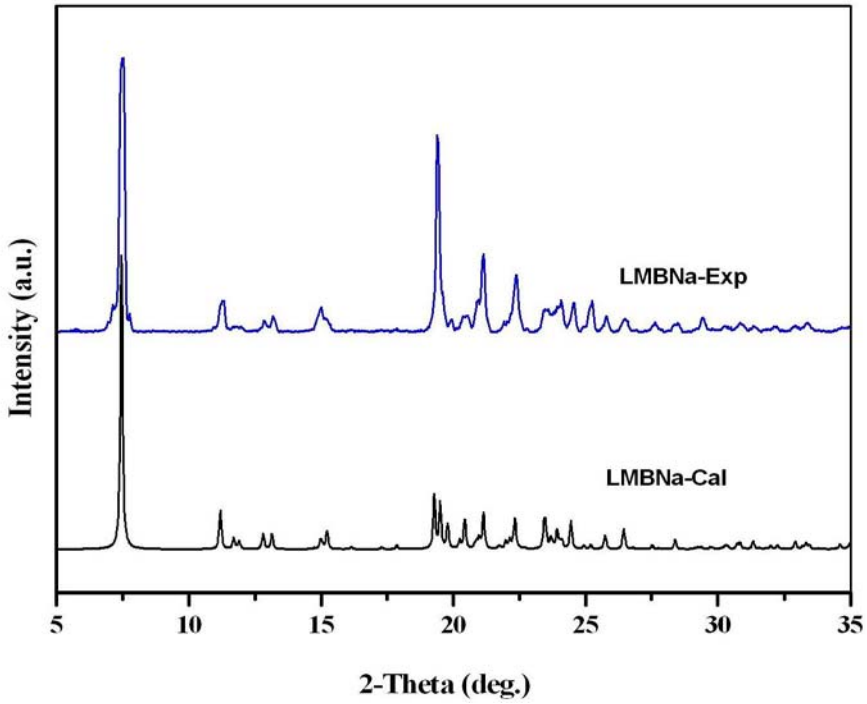

Figure S3. Experimental and calculated X-ray powder diffraction patterns.

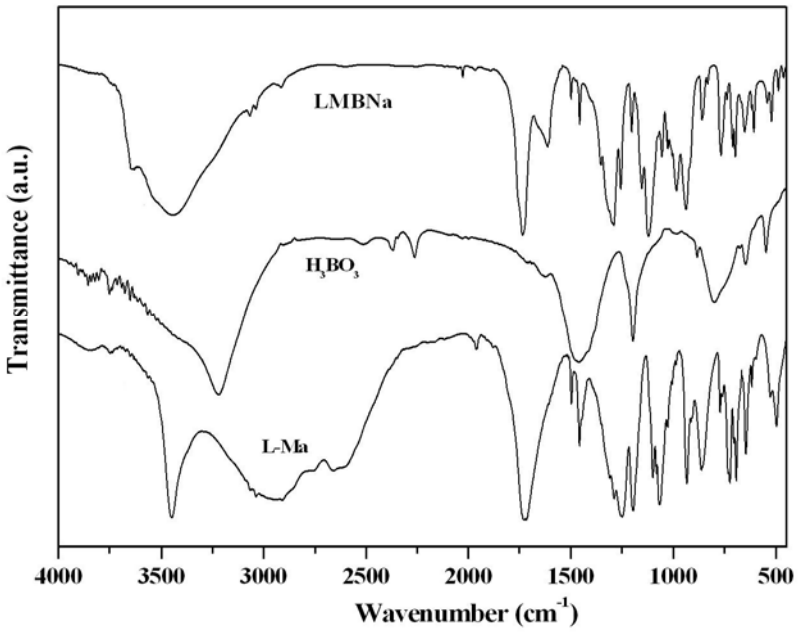

Figure S4. FT-IR spectra of LMBNa, H_3BO_3 and L-mandelic acid (L-Ma).

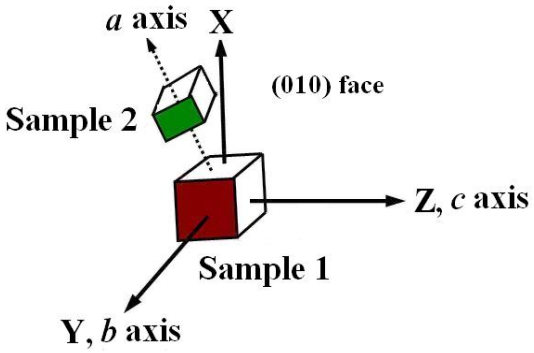

Figure S5. Schematic diagram of the samples for measuring the dielectric costant.

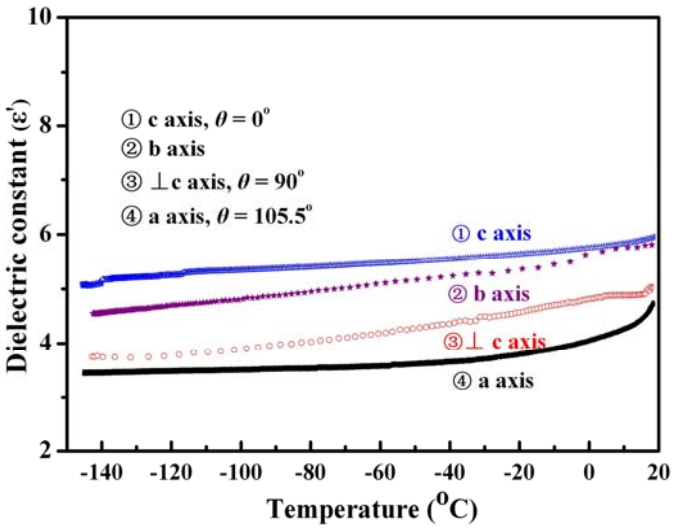

Figure S6. Dielectric constant vs temperature along different crystallographic directions at 1 MHz.