Supporting Information

New Ultraviolet Transparent Rare-Earth Borates with Enhanced Birefringence Iinduced by Cation Chemical Substitution

Guanglian Sun,[†] Xiaofang Qi,[†] WuHongping Wu,[†*] Zhanggui Hu,[†] Jiyang Wang,[†] and Yicheng Wu[†]*

[†]Tianjin Key Laboratory of Functional Crystal Materials, Institute of Functional Crystal, Tianjin

University of Technology, Tianjin 300384, China.

CONTENTS

Experimental Procedures

Reagents

Li_2CO_3 (Aladdin Reagent Co., Ltd, 99%), Na_2CO_3 (Macklin Reagent Co., Ltd, 99.5%), Rb_2CO_3 (Shanghai Industrial Co., Ltd, 99.9%), Cs_2CO_3 (Shanghai Industrial Co., Ltd, 99.9%), $SrCO_3$ (Macklin Reagent Co., Ltd, 99.5%), Y_2O_3 (Aladdin Reagent Co., Ltd, 99.99%), H_3BO_3 (Aladdin Reagent Co., Ltd, 99.5%) were obtained from commercial sources and utilized without further purification.

Synthesis

The polycrystalline samples were synthesized through conventional solid-state reactions. Stoichiometric amounts of Li_2CO_3, Na_2CO_3, Rb_2CO_3, $SrCO_3$, Y_2O_3 and H_3BO_3 were thoroughly ground and placed in platinum crucibles. The mixture were heated at 400°C for 10 h to facilitate the decomposition of H_2O and CO_2. Then the temperature was gradually raised to 800°C for $LiNa_2Y(BO_3)_2$, $RbSrY(BO_3)_2$ and 700°C for $RbNa_2Y(BO_3)_2$ and held for 48h with several intermittent grindings. Powder X-ray diffraction (XRD) analysis confirmed the successful synthesis of pure powders corresponding to these three compounds.

Crystal Growth

The single crystals were prepared using a high-temperature solution method. For $LiNa_2Y(BO_3)_2$, a mixture of Li_2CO_3 (0.0722g), Na_2CO_3 (0.1224 g), Cs_2CO_3 (0.6364g), Y_2O_3 (0.1103g), and H_3BO_3 (0.1812g) was placed in a vertical programmable temperature furnace. Then, the furnace was heated to 830 °C and kept for 2 h to ensure complete and homogeneous melting of the solution. Subsequently, the solution was slowly cooled to 650 °C at a rate of 5°C h^{-1}. Similarly, the crystals of $RbNa_2Y(BO_3)_2$ were obtained using the same temperature programs as that for $LiNa_2Y(BO_3)_2$ with a mixture of Rb_2CO_3 : Na_2CO_3 : Y_2O_3 : H_3BO_3 in the molar ratios of 4: 2 : 1 : 6. The Rb_2CO_3 (4mol), $SrCO_3$ (2mol),Y_2O_3 (1mol) and H_3BO_3 (6mol) were thoroughly mixed and then poured into a Pt crucible to prepare $RbSrY(BO_3)_2$. Then, the mixture was subjected to heating at 900 °C for 2 h followed by slow cooling at a rate of 5°C h^{-1} until reaching 750°C. Small crystals were obtained for structure determination. A large number of single crystals of micron scale were obtained and used for structure determination.

Single Crystal X-ray Diffraction

Single-crystal data was collected on a Bruker SMART APEX III 4 K CCD diffractometer using Mo-$K\alpha$ (λ =0.71073 Å) radiation at 293(2) K. The structure of three crystals were solved directly by the SHELXTL crystallographic software package and all atoms were refined by the full-matrix least squares technique. The final structures were examined for the presencce of any missing symmetry elements using PLATON, and no additional higher symmetry elements were identified. The crystal data and structure refinement details are listed in Table S1 and the atomic coordination, displacement parameters, bond valence sums (BVSs), and selected bond lengths and angles are summarized in Tables S2 and S3.

Powder X-ray Diffraction

Powder X-ray diffraction (PXRD) measurements for three polycrystalline materials were performed on a Smart Lab 9KW X-ray diffffractometer equipped with Cu Kα radiation (λ = 1.540598 Å) at room temperature, and the data were acquired through the 2θ angular range of 10-70° with a scan step width of 0.01° and a step time of 2s.

The powder XRD patterns of all compounds showed good agreement with the calculated XRD patterns from the single-crystal models (Fig. S4).

Infrared Spectroscopy

The infrared (IR) spectra were recorded using a Nicolet iS50 FT-IR spectrometer at room temperature in the range of 500-4000 cm^{-1} for $LiNa_2Y(BO_3)_2$ and $RbNa_2Y(BO_3)_2$, 500-3000 cm^{-1} for $RbSrY(BO_3)_2$.

UV-vis-NIR Diffuse Reflectance Spectroscopy and Transmission Spectrum

Reflectance spectra of the three compounds were collected using a Hitachi UV-VIS-NIR spectrophotometer in the range 190-2000 nm at room temperature. The Kubelka-Munk function: $F(R) = (1-R)^2 / 2R = K/S$ (where R represents the reflectance, K is the absorption, and S is the scattering) was used to convert the reflectance spectra to the absorbance data.

Thermal Stability

Differential scanning calorimetry (DSC) were measured by a STA449F5 DSC analyser (NETZSCH Instruments). The samples were placed in a platinum crucible and heated at a rate of 5 °C/min from room temperature to 900 °C, then cooled down to room temperature with the cooling rate of 5 °C/min under a nitrogen atmosphere.

The Birefringence Measurement

The birefringence of three crystals was determined by employing a Nikon Eclipse polarizing microscope E200MV POL equipped with a visible-light filter. Following the equation: $R = \Delta n \times d$ (where R, Δn, and d represents the optical path difference, birefringence and thickness, respectively).

Caculation Details

First-principle calculations on the electronic structures and optical properties of these three compounds were carried out using the total energy plane-wave pseudopotential method implemented in the CASTEP module in the Masterial Studio 7.0. The Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation was adopted as the exchange–correlation potential during the calculation. The following electrons were treated as valence electrons: Li $2s^1$, Na $2p^6\ 3s^1$, Rb $4s^2\ 4p^6\ 5s^1$, Sr $4s^2\ 4p^6\ 5s^2$, Y $4d^1\ 5s^2$, B $2s^2\ 2p^1$, O $2s^2\ 2p^4$, and O $2s^2\ 2p^4$. The plane-wave basis set energy cutoff was set at 810.0eV for $LiNa_2Y(BO_3)_2$, $RbNa_2Y(BO_3)_2$, and $RbSrY(BO_3)_2$ compounds. The k point sampling in the Brilliouin zone was set as $5 \times 4 \times 3$, $4 \times 5 \times 3$ and $5 \times 6 \times 4$ for $LiNa_2Y(BO_3)_2$, $RbNa_2Y(BO_3)_2$, and $RbSrY(BO_3)_2$. Our test showed that these parameters make good convergence in the present studies.

The linear-optical properties for these three compounds were obtained through the dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. The imaginary part of the dielectric function ε_2 is illustrated in the following equation:

$$\varepsilon_2\left(q \to O_u, h\omega\right) = \frac{2e^2\pi}{\Omega\varepsilon_0}\sum_{kcv}\left|\left\langle\varphi_k^c|\mathbf{u}\cdot\mathbf{r}|\varphi_k^v\right\rangle\right|^2\delta\left[E_k^c - E_k^v - E\right]$$

(Where e represents the elementary charge, h represents Planck's constant, $\mathbf{u}$ represents the vector of the incident polarization, $\mathbf{r}$ represents the position operator, Ω represents the unit cell volume, ε_0 represents the dielectric

constant, and φ_k represents the momentum matrix element transition.) The energies of occupied and empty electronic states use E_k^v and E_k^c, respectively. On the basis of the imaginary part, the real part can be obtained using the Kramers−Kronig transformation. Then the refractive index and the birefringence was obtained from the realpart of the dielectric function.

In addition, the electronic population was calculated by LCAO-MO Molecular Wave Functions as implanted in the Mulliken population analysis method.

Table S1 Crystal data and structure refinements for three compounds.

Empirical formula	LiNa$_2$Y(BO$_3$)$_2$	RbNa$_2$Y(BO$_3$)$_2$	RbSrY(BO$_3$)$_2$
Formula weight (g/mol)	259.44	337.97	379.62
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P\,2_1/n$	$Pnma$	$P\,2_1/m$
Z	4	8	2
	a = 6.321(4) Å	a=8.6912(15) Å	a=6.639(4) Å
Unit cell dimensions	b = 8.886(5) Å	b=6.8243(14) Å	b=5.404(3) Å
	c = 9.707(5) Å	c=11.0304(17) Å	c=8.592(5) Å
	β = 97.37(2)°		B = 105.560(18)°
V (Å3)	540.7(6)	654.2(2)	297.0(3)
Dc (g·cm-3)	3.187	3.431	4.246
Absorption coefficient(mm^{-1})	10.906	16.410	26.811
F(000)	488	624	344.0
Goodness-of-fit on F2	1.040	1.036	1.080
Independent reflections	1236	812	763
Rint	0.0584	0.087	0.0671
R1, wR2 (I >2σ(I))[a]	0.0298, 0.0668	0.0425,0.0962	0.0522,0.1306
R1, wR2 （all data）	0.0387,0.0707	0.0666,0.1064	0.0819,0.1485
Largest diff. peak and hole	0.576 and -0.926	1.401 and -1.057	1.512 and -1.706

[a]R1 = Σ||Fo|—|Fc||/Σ|Fo|. [b]wR2 = [Σw(Fo2—Fc2)2/Σw(Fo2)2]1/2.

Table S2 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3), U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)	BVS
			LiNa$_2$Y(BO$_3$)$_2$		
Y(1)	8403(1)	8403(1)	3505(1)	6(1)	3.09
Na(1)	-72(3)	2982(2)	976(2)	17(1)	1.02
Na(2)	1931(4)	4474(2)	3966(2)	44(1)	1.06
O(1)	7035(4)	3364(3)	2406(3)	9(1)	1.82
O(2)	1756(4)	2192(3)	3057(3)	14(1)	2.05
O(3)	4833(4)	626(3)	3198(3)	14(1)	2.03
O(4)	1756(4)	-116(3)	3198(3)	15(1)	1.93
O(5)	8053(5)	3190(3)	4847(3)	13(1)	2.01
O(6)	6557(5)	5489(3)	4847(3)	20(1)	1.99
B(1)	2830(7)	911(4)	3509(4)	20(1)	2.98
B(2)	7182(7)	4031(5)	3715(4)	10(1)	2.94
Li(1)	4257(13)	2552(9)	1694(7)	23(2)	0.96
			RbNa$_2$Y(BO$_3$)$_2$		
Y(1)	1309(1)	7500	6724(1)	11(1)	3.28
Rb(1)	5616(1)	7500	3580(1)	25(1)	1.11
Na(1)	8039(3)	9944(4)	5825(3)	18(1)	0.79
B(1)	4415(15)	7500	6258(11)	18(2)	2.89
B(2)	855(13)	2500	6115(10)	13(2)	2.98
O(1)	5998(8)	7500	6151(6)	20(2)	1.91
O(2)	3362(8)	7500	5345(6)	22(2)	1.97
O(3)	1288(6)	4232(7)	6647(5)	22(1)	2.01
O(4)	-6(9)	2500	5069(6)	22(2)	1.98
O(5)	3827(8)	7500	7455(6)	23(2)	2.01
			RbSrY(BO$_3$)$_2$		
Y(1)	7404(2)	7500	2480(1)	11(1)	3.26
Sr(1)	3222(2)	7500	4587(1)	15(1)	1.75
Rb(1)	1708(2)	7500	291(1)	19(1)	1.09
B(1)	10870(20)	2500	3530(14)	9(2)	3.01
B(2)	5760(20)	7500	-1750(16)	13(3)	3.01
O(1)	9988(10)	4706(12)	2891(8)	26(2)	2.01
O(2)	12522(13)	2500	4866(10)	21(2)	2.11

O(3)	6924(13)	7500	-188(10)	23(2)	2.14
O(4)	4935(9)	10316(11)	2534(7)	18(1)	2.09

Table S3 Selected bond distances (Å) and angles (deg.).

LiNa$_2$Y(BO$_3$)$_2$			
Y(1)-O(3)	2.266(3)	O(3)-Y(1)-O(6)#1	88.57(11)
Y(1)-O(6)#1	2.291(3)	O(3)-Y(1)-O(4)#2	84.75(10)
Y(1)-O(4)#2	2.338(3)	O(6)#1-Y(1)-O(4)#2	147.94(11)
Y(1)-O(5)	2.352(3)	O(3)-Y(1)-O(5)	92.12(10)
Y(1)-O(4)#3	2.375(3)	O(6)#1-Y(1)-O(5)	136.34(9)
Y(1)-O(1)	2.447(3)	O(4)#2-Y(1)-O(5)	75.34(10)
Y(1)-O(2)#3	2.450(3)	O(3)-Y(1)-O(4)#3	144.01(10)
Y(1)-O(1)#1	2.523(3)	O(6)#1-Y(1)-O(4)#3	95.04(11)
Na(1)-O(2)	2.303(3)	O(4)#2-Y(1)-O(4)#3	73.38(11)
Na(1)-O(6)#4	2.427(3)	O(5)-Y(1)-O(4)#3	108.91(10)
Na(1)-O(1)#5	2.457(3)	O(3)-Y(1)-O(1)	77.53(10)
Na(1)-O(3)#6	2.480(3)	O(6)#1-Y(1)-O(1)	78.29(10)
Na(1)-O(5)#7	2.597(3)	O(4)#2-Y(1)-O(1)	130.11(9)
Na(1)-O(4)#6	2.723(3)	O(5)-Y(1)-O(1)	59.40(9)
Na(1)-O(3)#7	2.961(3)	O(4)#3-Y(1)-O(1)	138.26(9)
Na(2)-O(2)	2.208(3)	O(3)-Y(1)-O(2)#3	155.82(10)
Na(2)-O(6)#8	2.254(4)	O(6)#1-Y(1)-O(2)#3	78.22(10)
Na(2)-O(5)#8	2.374(3)	O(4)#2-Y(1)-O(2)#3	116.96(10)
Na(2)-O(3)#6	2.470(4)	O(5)-Y(1)-O(2)#3	83.99(10)
Na(2)-O(5)#5	2.929(4)	O(4)#3-Y(1)-O(2)#3	58.40(10)
O(1)-B(2)	1.394(5)	O(1)-Y(1)-O(2)#3	79.99(10)
O(1)-Li(1)	1.942(9)	O(3)-Y(1)-O(1)#1	75.30(9)
O(2)-B(1)	1.368(5)	O(6)#1-Y(1)-O(1)#1	58.60(9)
O(2)-Li(1)	2.211(8)	O(4)#2-Y(1)-O(1)#1	89.40(10)
O(3)-B(1)	1.362(5)	O(5)-Y(1)-O(1)#1	161.19(9)
O(3)-Li(1)	2.248(8)	O(4)#3-Y(1)-O(1)#1	76.24(10)
O(4)-B(1)	1.391(5)	O(1)-Y(1)-O(1)#1	128.80(4)
O(4)-Li(1)#4	2.322(8)	O(2)#3-Y(1)-O(1)#1	113.18(9)
O(5)-B(2)	1.383(5)	O(2)-Na(1)-O(6)#4	78.47(11)
O(5)-Li(1)#9	1.970(8)	O(2)-Na(1)-O(1)#5	82.71(11)
O(6)-B(2)	1.360(5)	O(6)#4-Na(1)-O(1)#5	75.60(10)
O(2)-Na(1)-O(3)#6	90.13(11)	O(5)#8-Na(2)-O(3)#6	91.37(12)
O(6)#4-Na(1)-O(3)#6	147.57(12)	O(2)-Na(2)-O(5)#5	76.00(11)

O(1)#5-Na(1)-O(3)#6	72.87(10)	O(6)#8-Na(2)-O(5)#5	89.57(13)
O(2)-Na(1)-O(5)#7	85.69(11)	O(5)#8-Na(2)-O(5)#5	98.66(11)
O(6)#4-Na(1)-O(5)#7	89.74(11)	O(3)#6-Na(2)-O(5)#5	96.10(12)
O(1)#5-Na(1)-O(5)#7	162.85(10)	O(3)-B(1)-O(2)	121.4(3)
O(3)#6-Na(1)-O(5)#7	119.87(11)	O(3)-B(1)-O(4)	121.4(3)
O(2)-Na(1)-O(4)#6	87.40(11)	O(2)-B(1)-O(4)	117.2(3)
O(6)#4-Na(1)-O(4)#6	152.17(12)	O(6)-B(2)-O(5)	123.7(4)
O(1)#5-Na(1)-O(4)#6	126.58(11)	O(6)-B(2)-O(1)	118.3(3)
O(3)#6-Na(1)-O(4)#6	54.73(9)	O(5)-B(2)-O(1)	117.9(3)
O(5)#7-Na(1)-O(4)#6	65.16(10)	O(1)-Li(1)-O(5)#7	132.4(4)
O(2)-Na(1)-O(3)#7	151.06(12)	O(1)-Li(1)-O(2)	121.6(4)
O(6)#4-Na(1)-O(3)#7	119.98(10)	O(5)#7-Li(1)-O(2)	105.9(4)
O(1)#5-Na(1)-O(3)#7	121.80(10)	O(1)-Li(1)-O(3)	89.3(3)
O(3)#6-Na(1)-O(3)#7	83.79(10)	O(5)#7-Li(1)-O(3)	110.4(4)
O(5)#7-Na(1)-O(3)#7	73.18(9)	O(2)-Li(1)-O(3)	64.6(2)
O(4)#6-Na(1)-O(3)#7	66.02(9)	O(1)-Li(1)-O(4)#6	90.0(3)
Li(1)-Na(1)-O(3)#7	101.04(17)	O(5)#7-Li(1)-O(4)#6	83.4(3)
O(2)-Na(2)-O(6)#8	113.03(13)	O(2)-Li(1)-O(4)#6	100.5(3)
O(2)-Na(2)-O(5)#8	173.63(14)	O(3)-Li(1)-O(4)#6	161.6(4)
O(6)#8-Na(2)-O(5)#8	62.95(11)	O(6)#8-Na(2)-O(3)#6	154.28(13)
O(2)-Na(2)-O(3)#6	92.67(12)		

RbNa$_2$Y(BO$_3$)$_2$	

Y(1)-O(3)	2.232(4)	O(3)-Y(1)-O(3)#1	175.5(3)
Y(1)-O(3)#1	2.232(4)	O(3)-Y(1)-O(4)#2	87.86(13)
Y(1)-O(4)#2	2.279(7)	O(3)#1-Y(1)-O(4)#2	87.86(13)
Y(1)-O(5)	2.332(7)	O(3)-Y(1)-O(5)	91.21(14)
Y(1)-O(5)#3	2.340(7)	O(3)#1-Y(1)-O(5)	91.21(14)
Y(1)-O(2)	2.344(7)	O(4)#2-Y(1)-O(5)	140.0(3)
Y(1)-O(1)#3	2.360(7)	O(3)-Y(1)-O(5)#3	90.41(14)
Rb(1)-O(2)	2.762(7)	O(3)#1-Y(1)-O(5)#3	90.41(14)
Rb(1)-O(1)	2.855(7)	O(4)#2-Y(1)-O(5)#3	83.0(3)
Rb(1)-O(3)#7	2.947(5)	O(5)-Y(1)-O(5)#3	137.00(4)
Rb(1)-O(3)#8	2.947(5)	O(3)-Y(1)-O(2)	88.95(14)
Rb(1)-O(3)#9	2.950(5)	O(3)#1-Y(1)-O(2)	88.94(14)
Rb(1)-O(3)#10	2.950(5)	O(4)#2-Y(1)-O(2)	79.4(3)

Rb(1)-O(5)#10	3.631(2)	O(5)-Y(1)-O(2)	60.7(2)
Na(1)-O(1)	2.461(6)	O(5)#3-Y(1)-O(2)	162.3(2)
Na(1)-O(2)#5	2.488(5)	O(3)-Y(1)-O(1)#3	92.12(13)
Na(1)-O(4)#11	2.574(7)	O(3)#1-Y(1)-O(1)#3	92.12(13)
Na(1)-O(4)#10	2.584(7)	O(4)#2-Y(1)-O(1)#3	143.6(3)
Na(1)-O(5)#12	2.617(6)	O(5)-Y(1)-O(1)#3	76.4(2)
Na(1)-O(3)#9	2.831(6)	O(5)#3-Y(1)-O(1)#3	60.6(2)
Na(1)-O(3)#13	3.019(6)	O(2)-Y(1)-O(1)#3	137.0(2)
B(1)-O(2)	1.361(14)	O(2)-Rb(1)-O(1)	51.9(2)
B(1)-O(1)	1.381(14)	O(2)-Rb(1)-O(3)#7	96.43(16)
B(1)-O(5)	1.415(13)	O(1)-Rb(1)-O(3)#7	141.65(15)
B(2)-O(3)#14	1.372(7)	O(2)-Rb(1)-O(3)#8	96.43(16)
B(2)-O(3)	1.372(7)	O(1)-Rb(1)-O(3)#8	141.65(15)
B(2)-O(4)	1.375(13)	O(3)#7-Rb(1)-O(3)#8	47.29(18)
O(1)-Na(1)-O(2)#5	101.4(2)	O(2)-Rb(1)-O(3)#9	134.98(15)
O(1)-Na(1)-O(4)#11	169.2(2)	O(1)-Rb(1)-O(3)#9	88.75(17)
O(2)#5-Na(1)-O(4)#11	71.3(2)	O(3)#7-Rb(1)-O(3)#9	127.70(10)
O(1)-Na(1)-O(4)#10	95.47(19)	O(3)#8-Rb(1)-O(3)#9	106.87(12)
O(2)#5-Na(1)-O(4)#10	125.3(2)	O(2)-Rb(1)-O(3)#10	134.98(15)
O(4)#11-Na(1)-O(4)#10	82.92(9)	O(1)-Rb(1)-O(3)#10	88.75(17)
O(1)-Na(1)-O(5)#12	69.6(2)	O(3)#7-Rb(1)-O(3)#10	106.87(12)
O(2)#5-Na(1)-O(5)#12	162.0(3)	O(3)#8-Rb(1)-O(3)#10	127.70(10)
O(4)#11-Na(1)-O(5)#12	119.6(2)	O(3)#9-Rb(1)-O(3)#10	47.23(18)
O(4)#10-Na(1)-O(5)#12	72.1(2)	O(2)-Rb(1)-O(1)	51.9(2)
O(1)-Na(1)-O(3)#9	100.0(2)	O(2)-Rb(1)-O(3)#7	96.43(16)
O(2)#5-Na(1)-O(3)#9	73.83(19)	O(1)-Rb(1)-O(3)#7	141.65(15)
O(4)#11-Na(1)-O(3)#9	70.59(18)	O(2)-Rb(1)-O(3)#8	96.43(16)
O(4)#10-Na(1)-O(3)#9	52.03(18)	O(1)-Rb(1)-O(3)#8	141.65(15)
O(5)#12-Na(1)-O(3)#9	122.32(19)	O(3)#7-Rb(1)-O(3)#8	47.29(18)
O(1)-Na(1)-O(3)#13	139.18(19)	O(2)-B(1)-O(1)	127.4(10)
O(2)#5-Na(1)-O(3)#13	118.86(18)	O(2)-B(1)-O(5)	116.6(10)
O(4)#11-Na(1)-O(3)#13	49.72(18)	O(1)-B(1)-O(5)	116.1(10)
O(4)#10-Na(1)-O(3)#13	67.41(18)	O(3)#14-B(2)-O(3)	119.0(9)
O(5)#12-Na(1)-O(3)#13	69.90(18)	O(3)#14-B(2)-O(4)	120.5(4)
O(3)#9-Na(1)-O(3)#13	97.33(16)	O(3)-B(2)-O(4)	120.5(4)

RbSrY(BO₃)₂			
Y(1)-O(3)	2.228(9)	O(3)-Y(1)-O(1)	93.1(2)
Y(1)-O(1)	2.241(6)	O(3)-Y(1)-O(1)#1	93.1(2)
Y(1)-O(1)#1	2.241(7)	O(1)-Y(1)-O(1)#1	84.7(3)
Y(1)-O(4)	2.246(6)	O(3)-Y(1)-O(4)	96.7(2)
Y(1)-O(4)#1	2.246(6)	O(1)-Y(1)-O(4)	170.2(2)
Y(1)-O(2)#2	2.267(9)	O(1)#1-Y(1)-O(4)	94.1(2)
Sr(1)-O(1)#7	2.709(6)	O(3)-Y(1)-O(4)#1	96.7(2)
Sr(1)-O(1)#8	2.709(6)	O(1)-Y(1)-O(4)#1	94.1(2)
Sr(1)-O(4)#5	2.717(6)	O(1)#1-Y(1)-O(4)#1	170.2(2)
Sr(1)-O(4)#9	2.717(6)	O(4)-Y(1)-O(4)#1	85.3(3)
Sr(1)-O(2)#2	2.737(9)	O(3)-Y(1)-O(2)#2	173.3(3)
Sr(1)-O(2)#7	2.763(2)	O(1)-Y(1)-O(2)#2	91.9(2)
Sr(1)-O(2)#10	2.763(2)	O(1)#1-Y(1)-O(2)#2	91.9(2)
Sr(1)-O(4)	2.793(6)	O(4)-Y(1)-O(2)#2	78.4(2)
Sr(1)-O(4)#1	2.793(6)	O(4)#1-Y(1)-O(2)#2	78.4(2)
Rb(1)-O(3)#4	2.859(3)	O(1)#7-Sr(1)-O(1)#8	67.8(3)
Rb(1)-O(3)#3	2.859(3)	O(1)#7-Sr(1)-O(4)#5	146.1(2)
Rb(1)-O(4)#1	2.899(6)	O(1)#8-Sr(1)-O(4)#5	110.25(17)
Rb(1)-O(4)	2.899(6)	O(1)#7-Sr(1)-O(4)#9	110.25(17)
Rb(1)-O(1)#3	2.917(7)	O(1)#8-Sr(1)-O(4)#9	146.1(2)
Rb(1)-O(1)#12	2.917(7)	O(4)#5-Sr(1)-O(4)#9	51.5(2)
Rb(1)-O(3)#7	3.091(9)	O(1)#7-Sr(1)-O(2)#2	136.48(17)
Rb(1)-O(1)#8	3.153(7)	O(1)#8-Sr(1)-O(2)#2	136.48(17)
Rb(1)-O(1)#7	3.153(7)	O(4)#5-Sr(1)-O(2)#2	69.6(2)
B(1)-O(2)	1.360(13)	O(4)#9-Sr(1)-O(2)#2	69.6(2)
B(1)-O(1)#13	1.375(8)	O(1)#7-Sr(1)-O(2)#7	51.2(2)
B(1)-O(1)	1.375(8)	O(1)#8-Sr(1)-O(2)#7	117.7(2)
B(2)-O(3)	1.356(14)	O(4)#5-Sr(1)-O(2)#7	113.0(2)
B(2)-O(4)#14	1.376(8)	O(4)#9-Sr(1)-O(2)#7	62.7(2)
B(2)-O(4)#4	1.376(8)	O(2)#2-Sr(1)-O(2)#7	100.08(17)
O(3)#4-Rb(1)-O(3)#3	141.8(3)	O(1)#7-Sr(1)-O(2)#10	117.7(2)
O(3)#4-Rb(1)-O(4)#1	109.4(2)	O(1)#8-Sr(1)-O(2)#10	51.2(2)
O(3)#3-Rb(1)-O(4)#1	48.7(2)	O(4)#5-Sr(1)-O(2)#10	62.7(2)
O(3)#4-Rb(1)-O(4)	48.7(2)	O(4)#9-Sr(1)-O(2)#10	113.0(2)

O(3)#3-Rb(1)-O(4)	109.4(2)	O(2)#2-Sr(1)-O(2)#10	100.08(18)
O(4)#1-Rb(1)-O(4)	63.3(2)	O(2)#7-Sr(1)-O(2)#10	155.9(4)
O(3)#4-Rb(1)-O(1)#3	113.8(2)	O(1)#7-Sr(1)-O(4)	111.24(18)
O(3)#3-Rb(1)-O(1)#3	68.3(2)	O(1)#8-Sr(1)-O(4)	75.79(19)
O(4)#1-Rb(1)-O(1)#3	116.04(16)	O(4)#5-Sr(1)-O(4)	100.26(16)
O(4)-Rb(1)-O(1)#3	150.22(19)	O(4)#9-Sr(1)-O(4)	130.66(10)
O(3)#4-Rb(1)-O(1)#12	68.3(2)	O(2)#2-Sr(1)-O(4)	62.08(19)
O(3)#3-Rb(1)-O(1)#12	113.8(2)	O(2)#7-Sr(1)-O(4)	134.0(2)
O(4)#1-Rb(1)-O(1)#12	150.22(19)	O(2)#10-Sr(1)-O(4)	68.2(2)
O(4)-Rb(1)-O(1)#12	116.04(16)	O(1)#7-Sr(1)-O(4)#1	75.79(19)
O(1)#3-Rb(1)-O(1)#12	48.2(3)	O(1)#8-Sr(1)-O(4)#1	111.24(18)
O(3)#4-Rb(1)-O(3)#7	108.62(17)	O(4)#5-Sr(1)-O(4)#1	130.66(10)
O(3)#3-Rb(1)-O(3)#7	108.62(17)	O(4)#9-Sr(1)-O(4)#1	100.26(16)
O(4)#1-Rb(1)-O(3)#7	129.66(17)	O(2)#2-Sr(1)-O(4)#1	62.08(19)
O(4)-Rb(1)-O(3)#7	129.66(17)	O(2)#7-Sr(1)-O(4)#1	68.2(2)
O(1)#3-Rb(1)-O(3)#7	75.57(19)	O(2)#10-Sr(1)-O(4)#1	134.0(2)
O(1)#12-Rb(1)-O(3)#7	75.57(19)	O(4)-Sr(1)-O(4)#1	66.0(2)
O(3)#4-Rb(1)-O(1)#8	75.4(2)	O(1)#3-Rb(1)-O(1)#7	110.25(14)
O(3)#3-Rb(1)-O(1)#8	130.8(2)	O(1)#12-Rb(1)-O(1)#7	137.52(9)
O(4)#1-Rb(1)-O(1)#8	97.13(17)	O(3)#7-Rb(1)-O(1)#7	62.60(18)
O(4)-Rb(1)-O(1)#8	67.75(18)	O(1)#8-Rb(1)-O(1)#7	57.2(2)
O(1)#3-Rb(1)-O(1)#8	137.52(9)	O(2)-B(1)-O(1)#13	119.8(5)
O(1)#12-Rb(1)-O(1)#8	110.25(14)	O(2)-B(1)-O(1)	119.8(5)
O(3)#7-Rb(1)-O(1)#8	62.60(18)	O(1)#13-B(1)-O(1)	120.1(10)
O(3)#4-Rb(1)-O(1)#7	130.8(2)	O(3)-B(2)-O(4)#14	120.8(5)
O(3)#3-Rb(1)-O(1)#7	75.4(2)	O(3)-B(2)-O(4)#4	120.8(5)
O(4)#1-Rb(1)-O(1)#7	67.75(18)	O(4)#14-B(2)-O(4)#4	118.1(10)
O(4)-Rb(1)-O(1)#7	97.13(17)		

Symmetry transformations used to generate equivalent atoms:

LiNa₂Y(BO₃)₂

#1 -x+3/2,y-1/2,-z+1/2   #2 -x+1,-y,-z+1   #3 x+1,y,z

#4 -x+1/2,y-1/2,-z+1/2   #5 x-1,y,z   #6 -x+1/2,y+1/2,-z+1/2

#7 x-1/2,-y+1/2,z-1/2   #8 -x+1,-y+1,-z+1   #9 x+1/2,-y+1/2,z+1/2

#10 -x+3/2,y+1/2,-z+1/2

RbNa₂Y(BO₃)₂

#1 x,-y+3/2,z   #2 -x,-y+1,-z+1   #3 x-1/2,y,-z+3/2

#4 -x+1,y-1/2,-z+1   #5 -x+1,-y+2,-z+1   #6 x-1,-y+3/2,z

#7 -x+1/2,-y+1,z-1/2   #8 -x+1/2,y+1/2,z-1/2   #9 -x+1,y+1/2,-z+1

#10 -x+1,-y+1,-z+1   #11 x+1,y+1,z   #12 x+1/2,y,-z+3/2

#13 x+1,-y+3/2,z   #14 x,-y+1/2,z   #15 x+1,y,z

#16 -x+1/2,-y+1,z+1/2   #17 x-1,y-1,z   #18 x-1/2,-y+3/2,-z+3/2

RbSrY(BO₃)₂

#1 x,-y+3/2,z   #2 -x+2,-y+1,-z+1   #3 -x+1,-y+1,-z

#4 -x+1,-y+2,-z   #5 -x+1,-y+2,-z+1   #6 -x+1,-y+1,-z+1

#7 x-1,y,z   #8 x-1,-y+3/2,z   #9 -x+1,y-1/2,-z+1

#10 x-1,y+1,z   #11 x,y,z+1   #12 -x+1,y+1/2,-z

#13 x,-y+1/2,z   #14 -x+1,y-1/2,-z   #15 x+1,y,z

#16 x+1,y-1,z   #17 x,y,z-1

Table S4 Summary of Y-based borates with isolated BO_3.

Compound	Space group	Birefringence	$\lambda_{\text{cut-off}}$
$LiNa_2Y(BO_3)_2$[This work]	$P2_1/n$	0.017@532nm	<190nm
$RbNa_2Y(BO_3)_2$[This work]	$Pnma$	0.033@532nm	<190nm
$RbSrY(BO_3)_2$[This work]	$P2_1/m$	0.07@532nm	<190nm
$LiRb_2Y(BO_3)_2$	$Pbcm$	0038@532nm	<190nm
$CaRbY(BO_3)_2$	$Pbca$	0.048@532nm	<190nm
$YCa_4O(BO_3)_3$	Cm	0.04@532nm	200nm
$Na_3Y_3(BO_3)_4$	$P6_3mc$	0.035@400nm	/
$YAl_3(BO_3)_4$	$R32$	0.07@546nm	170nm
$Li_2RbY_4(BO_3)_5$	$P2/n$	0.10@532nm	<190nm
$Li_2CsY_4(BO_3)_5$	$P2/n$	0.10@532nm	<190nm
$LiCaY_5(BO_3)_6$	$P6_522$	/	/
$Na_2Y_2B_2O_7$	$P2_1/c$	/	/
$Li_3K_3Y_7(BO_3)_9$	$Pna2_1$	/	/
β-$Ba_3YB_3O_9$	R-3	/	/
α-$Ba_3YB_3O_9$	$P6_3cm$	/	/
$Li_3Y(BO_3)_2$	$P2_1/c$	/	/
$Li_2KY(BO_3)_2$	$P2_1/n$	/	/
$K_3Y(BO_3)_2$	$Pnnm$	/	/
$K_3Y_3(BO_3)_4$	$P2_1/c$	/	/
$Ba_2Y(BO_3)_2Cl$	$P2_1/m$	/	/
$Sr_3Y(BO_3)_3$	R-3	/	/
$Sr_3Y_2(BO_3)_4$	$Pc2_1n$	/	/
$Ba_3Y_2(BO_3)_4$	$Pnma$	/	/
$Li_6Y(BO_3)_3$	$P2_1/c$	/	/
$Rb_3Y_2(BO_3)_3$	$Pna2_1$	/	/
$CaYBO_4$	$Pnam$	/	/
$BaYOBO_3$	P-$62m$	/	<190nm
$KBaY(BO_3)_2$	R-$3m$	/	/
$KSrY(BO_3)_2$	$P2_1/m$	/	/

Table S5 Muliken bond population and selected bond distances of $LiNa_2Y(BO_3)_2$, $RbNa_2Y(BO_3)_2$, and $RbSrY(BO_3)_2$.

LiNa$_2$Y(BO$_3$)$_2$			RbNa$_2$Y(BO$_3$)$_2$			RbSrY(BO$_3$)$_2$		
Bond	Popu lation	Lengt h(Å)	Bond	Popu lation	Lengt h(Å)	Bond	Popu lation	Lengt h(Å)
B2-O6	0.93	1.360	B1-O2	0.92	1.361	B2-O3	0.91	1.357
B1-O3	0.90	1.362	B2-O3	0.92	1.372	B1-O2	0.81	1.358
B1-O2	0.90	1.368	B2-O3	0.92	1.372	B1-O1	0.83	1.376
B2-O5	0.87	1.383	B2-O4	0.85	1.375	B1-O1	0.83	1.376
B1-O4	0.85	1.391	B1-O1	0.90	1.381	B2-O4	0.85	1.376
B2-O1	0.85	1.394	B2-O5	0.82	1.416	B2-O4	0.85	1.376
Y1-O3	0.55	2.265	Y1-O3	0.55	2.232	Y1-O3	0.57	2.229
Y1-O6	0.27	2.291	Y1-O3	0.55	2.232	Y1-O1	0.48	2.241
Y1-O4	0.36	2.338	Y1-O4	0.41	2.379	Y1-O1	0.48	2.241
Y1-O5	0.28	2.353	Y1-O5	0.20	2.332	Y1-O4	0.46	2.246
Y1-O4	0.22	2.375	Y1-O5	0.21	2.340	Y1-O4	0.46	2.246
Y1-O1	0.22	2.447	Y1-O2	0.19	2.344	Y1-O2	0.33	2.267
Y1-O2	0.13	2.450	Y1-O1	0.18	2.360			
Y1-O1	0.17	2.524						
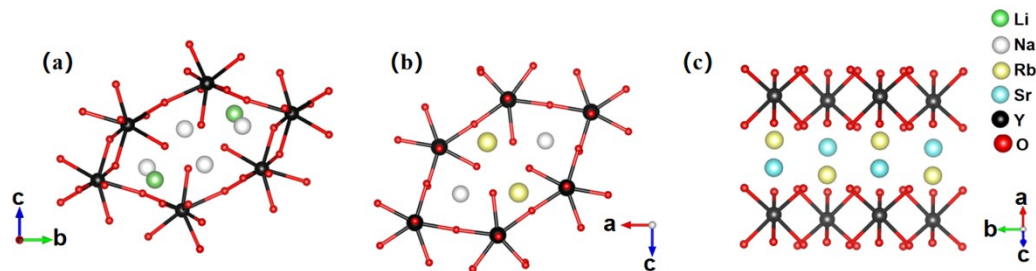
Fig. S1 The six membered rings in $LiNa_2Y(BO_3)_2$ (a) and $RbNa_2Y(BO_3)_2$ (b) or interlayer spaces in $RbSrY(BO_3)_2$ (c).
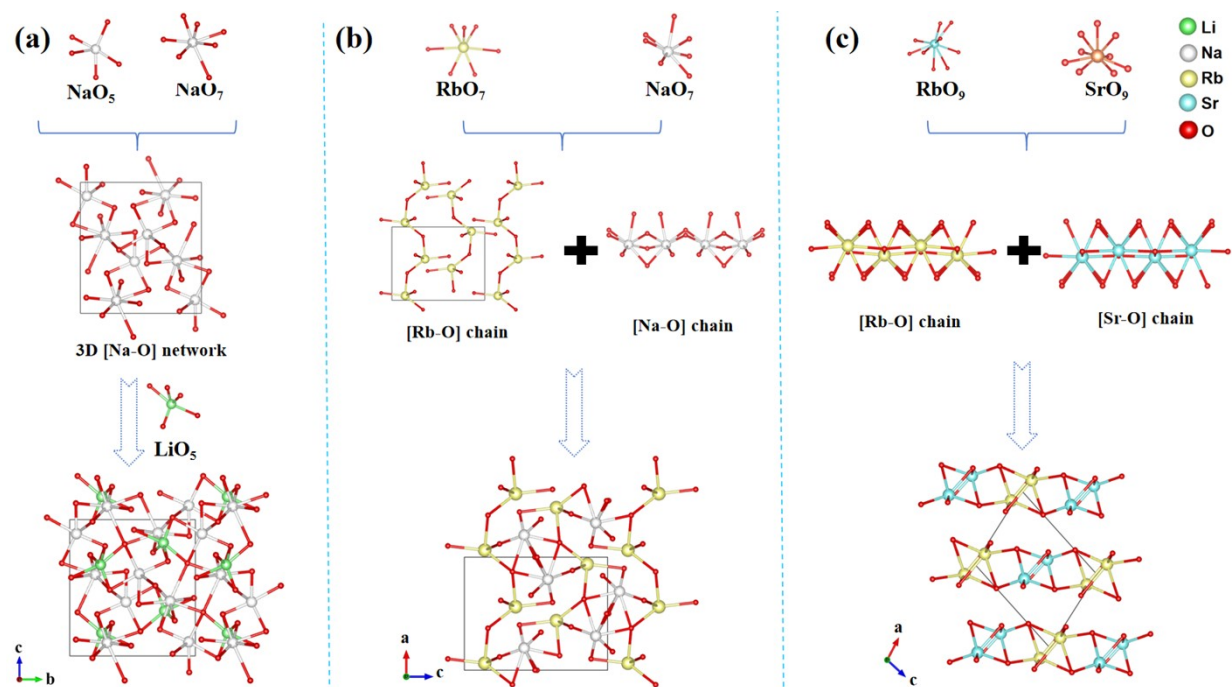
Fig. S2 Cation coordination environment linkage modes in LiNa$_2$Y(BO$_3$)$_2$(a), RbNa$_2$Y(BO$_3$)$_2$ (b), and RbSrY(BO$_3$)$_2$ (c).
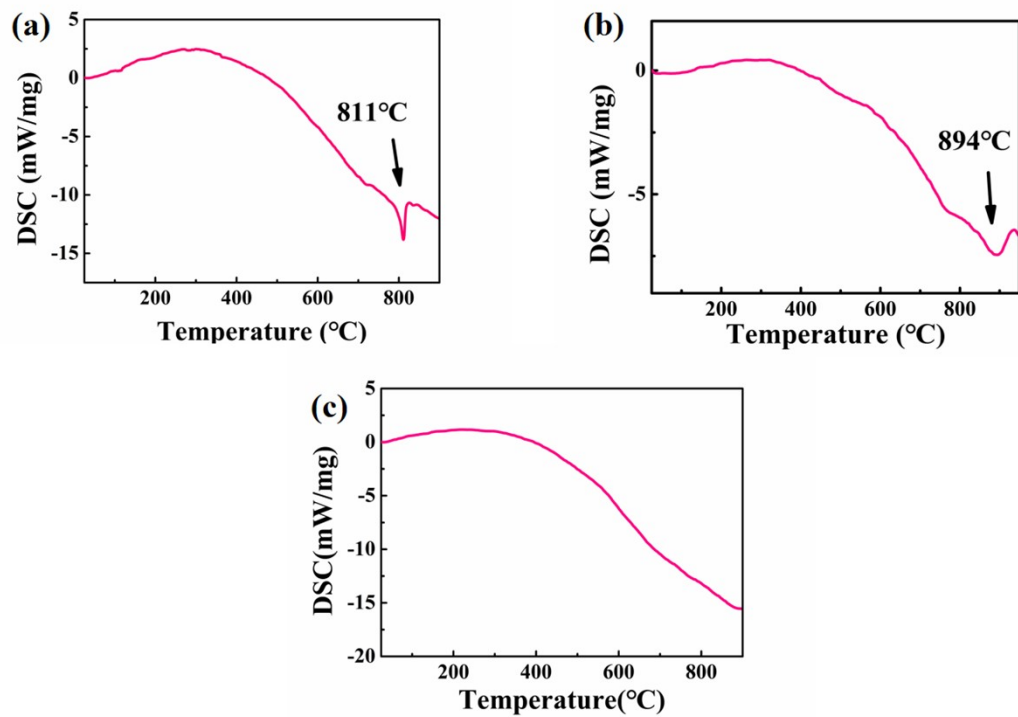
Fig. S3 DSC curves of LiNa$_2$Y(BO$_3$)$_2$ (a), RbiNa$_2$Y(BO$_3$)$_2$ (b), and RbSrY(BO$_3$)$_2$ (c).
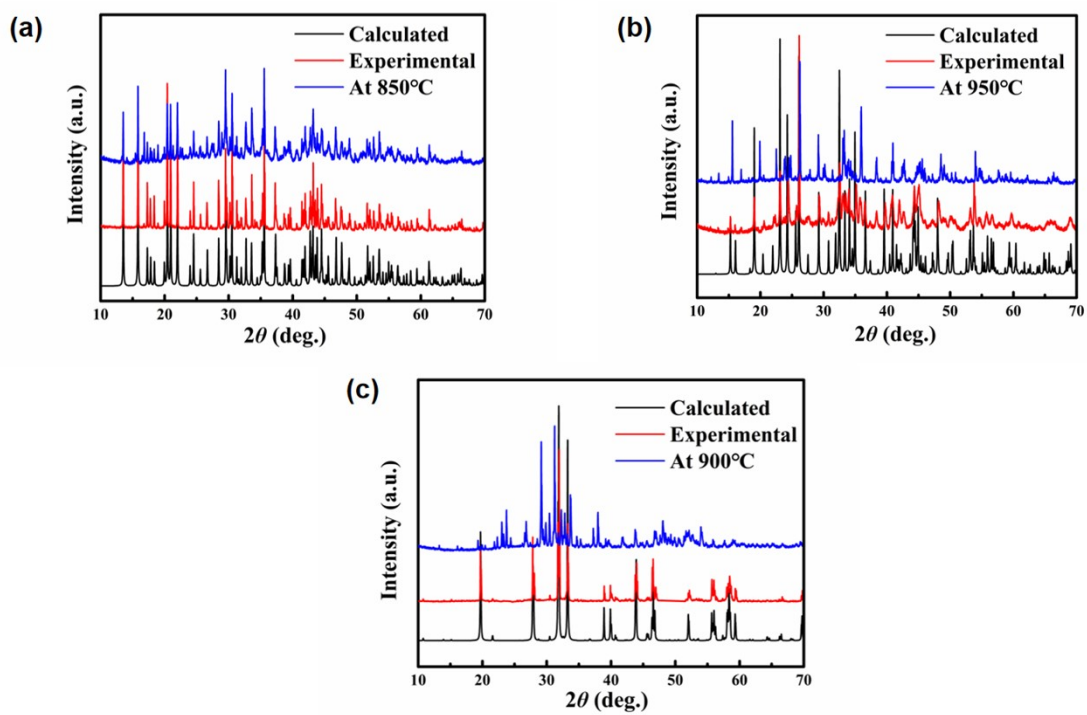
Fig. S4 X-ray powder diffraction patterns of LiNa$_2$Y(BO$_3$)$_2$ (a), RbiNa$_2$Y(BO$_3$)$_2$ (b), and RbSrY(BO$_3$)$_2$ (c).
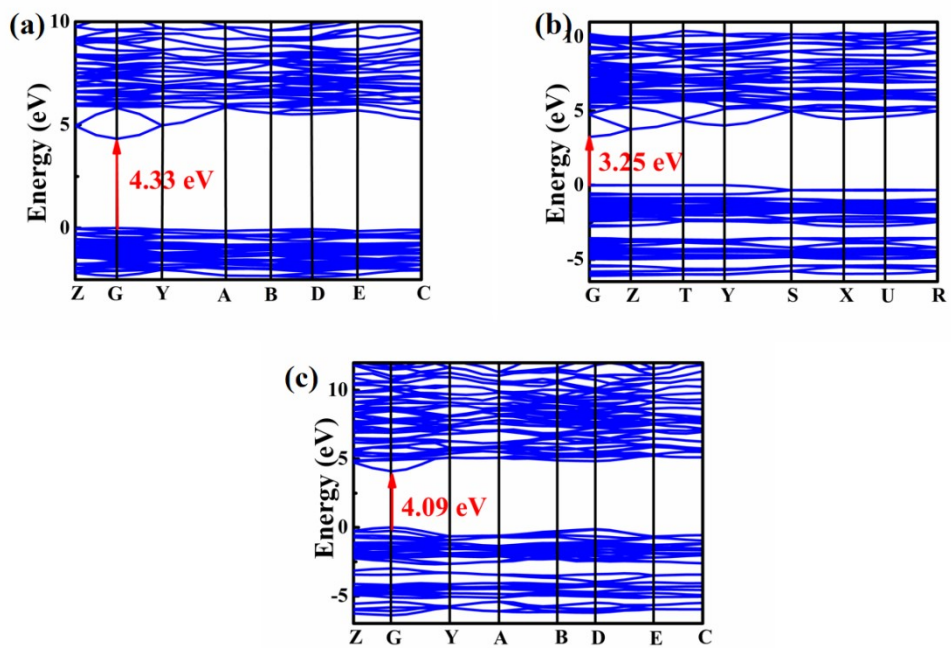
Fig. S5 Calculated band structures of $LiNa_2Y(BO_3)_2$(a), $RbNa_2Y(BO_3)_2$(b), and $RbSrY(BO_3)_2$ (c).
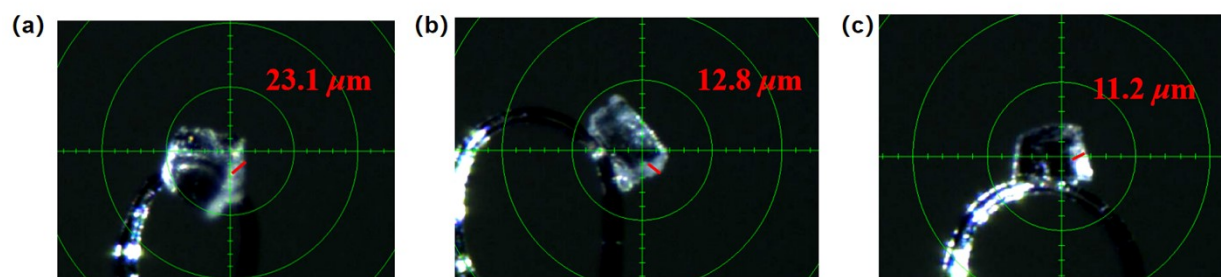
Fig. S6 Thickness of LiNa$_2$Y(BO$_3$)$_2$ (a), RbNa$_2$Y(BO$_3$)$_2$ (b), and RbSrY(BO$_3$)$_2$ (c).