Supporting Information

A Potential UV Nonlinear-Optical Crystal with Strong Second-Harmonic Response: $RbNa_2Eu_2(BO_3)_3$

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Experimental section

Polycrystalline powder synthesis: The RNEBO polycrystalline powder was synthesized by the traditional solid phase method in the Muffle furnace under the condition of not less than 710℃. Firstly, Rb_2CO_3 (Sinopharm, 99.9%), Eu_2O_3 (Sinopharm, 99.9%), H_3BO_3 (Sinopharm, 99.9%), Na_2CO_3 (Sinopharm, 99.9%) were mixed evenly and ground with mortar for not less than 30 minutes, and the grinding is taken out several times during sintering to obtain crystals. Powder X-ray diffraction characterization: The pure polycrystalline phase of RNEBO was determined by the traditional Rigaku SmartLab 9 kW diffractometer at room temperature with Cu Kα radiation (λ= 1.5418A) as the diffraction parameter. The test range was 10°-70° and the step length rate was 5°/min. UV spectrum characterization: Hitachi UH4150 spectrophotometer was used to test the UV-VIS diffuse reflection spectrum of RNEBO in the range of 190-2000nm with $BaSO_4$ was used as a blank control sample. Infrared spectrum characterization: The functional group behavior of RNEBO was tested with Shimadzu IR spectrometer in the wavelength range of 500-4000cm^{-1}. Thermal analysis: Thermogravimetric analysis of RNEBO polycrystalline powder was performed at 25-1200℃ with thermal mechanical analyzer (TMA402F3). Energy dispersive spectroscopy: The eds analyses of RNEBO were conducted with thermal field emission scanning electron microscopy (Gemini 500). Powder SHG

characterization: Polycrystalline powder SHG response of RNEBO had been measured by a Q-switched Nd: YAG solid state laser (1064 nm) with using the Kurtz−Perry method. Theoretical calculations were calculated through the CASTEP program by density functional theory (DFT).

Table S1. Crystal data and structure refinement for RNEBO.

Chemical formula	$RbNa_2Eu_2(BO_3)_3$
Formula weight	611.80 g/mol
Crystal system	orthorhombic
Temperature	273(2) K
Space group	Amm2
Unit cell dimensions	a = 5.1228(2) Å
	b = 11.1226(7) Å
	c = 7.0441(4) Å
Volume, Z	401.36(4) $Å^3$, 2
Density (calculated)	5.062 g/cm^3
Theta range for data collection	3.42 to 32.48°
Independent reflections	R(int) = 0.0371
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.149
Final R indices I>2σ(I)	R1 = 0.0346, wR2 = 0.0884
R indices (all data)	R1 = 0.0348, wR2 = 0.0885

[a] $R_1=\sum||F_0|-|F_c||/\sum|F_0|$ and $wR_2=[\sum w(F_0^2-F_c^2)^2/\sum w\ F_0^4]^{1/2}$ for $F_0^2>2\sigma(F_0^2)$

Table S2. Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for (RNEBO).

Atoms	x	y	z	U(eq)
Eu(1)	0.5	0.28661(6)	0.77467(17)	0.0068(3)
Na(1)	0.0	0.5	0.8714(16)	0.0051(12)
Rb(1)	0.0	0.5	0.3821(6)	0.0252(8)
Na(2)	0.5	0.5	0.1334(17)	0.0051(12)
O(1)	0.7628(17)	0.1596(9)	0.5642(15)	0.0078(17)
O(2)	0.5	0.5	0.748(4)	0.017(5)
O(3)	0.5	0.3923(12)	0.463(2)	0.0051(12)
O(4)	0.0	0.3236(17)	0.695(3)	0.020(3)
B(1)	0.5	0.5	0.549(5)	0.013(6)
B(2)	0.0	0.2162(17)	0.600(3)	0.0051(12)

Table S3. Bond lengths [Å] and Angles [°] for RNEBO. Operators for generating equivalent atoms.

Eu1-O2	2.381(2)	Eu1-O3	2.394(14)
Eu1-O1	2.450(10)	Eu1-O1	2.450(10)
Eu1-O3	2.488(15)	Eu1-O1	2.516(10)
Eu1-O1	2.516(10)	Eu1-O4	2.655(5)
Eu1-O4	2.655(5)	Eu1-B1	2.86(2)
Eu1-B2	2.947(11)	Eu1-B2	2.947(11)
Na1-O4	2.323(19)	Na1-O4	2.323(19)
Na1-O1	2.544(12)	Na1-O1	2.544(12)
Na1-O1	2.544(12)	Na1-O1	2.544(12)
Na1-O2	2.706(10)	Na1-O2	2.706(10)
Na1-B2	2.89(2)	Na1-B2	2.89(2)
Na1-Na2	3.157(10)	Na1-Na2	3.157(10)
Rb2-B1	2.817(16)	Rb2-B1	2.817(16)
Rb2-O3	2.885(6)	Rb2-O3	2.885(6)
Rb2-O3	2.885(6)	Rb2-O3	2.885(6)
Rb2-O4	2.95(2)	Rb2-O4	2.95(2)
Rb2-Na2	3.103(7)	Rb2-Na2	3.103(7)

Rb2-O1	3.106(11)	Rb2-O1	3.106(11)
Na2-O1	2.281(10)	Na2-O1	2.281(10)
Na2-O1	2.281(10)	Na2-O1	2.281(10)
Na2-O3	2.615(19)	Na2-O3	2.615(19)
Na2-O2	2.72(3)	Na2-B1	2.92(4)
O1-B2	1.392(13)	O2-B1	1.40(4)
O3-B1	1.34(2)	O4-B2	1.37(3)
Angles [°]			
O2-Eu1-O3	150.8(8)	O2-Eu1-O1	121.7(6)
O3-Eu1-O1	81.8(4)	O2-Eu1-O1	121.7(6)
O3-Eu1-O1	81.8(4)	O1-Eu1-O1	66.6(4)
O2-Eu1-O3	57.2(7)	O3-Eu1-O3	152.0(5)
O1-Eu1-O3	74.9(4)	O1-Eu1-O3	74.9(4)
O2-Eu1-O1	80.1(6)	O3-Eu1-O1	75.4(4)
O1-Eu1-O1	157.1(3)	O1-Eu1-O1	109.5(3)
O3-Eu1-O1	127.0(3)	O2-Eu1-O1	80.1(6)
O3-Eu1-O1	75.4(4)	O1-Eu1-O1	109.5(3)
O1-Eu1-O1	157.1(3)	O3-Eu1-O1	127.0(3)
O1-Eu1-O1	64.7(4)	O2-Eu1-O4	80.1(4)

O3-Eu1-O4	104.3(4)	O1-Eu1-O4	119.4(4)
O1-Eu1-O4	55.3(4)	O3-Eu1-O4	74.9(4)
O1-Eu1-O4	67.6(4)	O1-Eu1-O4	130.6(4)
O2-Eu1-O4	80.1(4)	O3-Eu1-O4	104.3(4)
O1-Eu1-O4	55.3(4)	O1-Eu1-O4	119.4(4)
O3-Eu1-O4	74.9(4)	O1-Eu1-O4	130.6(4)
O1-Eu1-O4	67.6(4)	O4-Eu1-O4	149.6(8)
O2-Eu1-B1	29.3(8)	O3-Eu1-B1	179.9(7)
O1-Eu1-B1	98.1(6)	O1-Eu1-B1	98.1(6)
O3-Eu1-B1	27.9(7)	O1-Eu1-B1	104.7(6)
O1-Eu1-B1	104.7(6)	O4-Eu1-B1	75.7(4)
O4-Eu1-B1	75.7(4)	O2-Eu1-B2	103.4(5)
O3-Eu1-B2	90.6(4)	O1-Eu1-B2	94.1(4)
O1-Eu1-B2	28.0(4)	O3-Eu1-B2	76.0(4)
O1-Eu1-B2	86.3(4)	O1-Eu1-B2	150.0(5)
O4-Eu1-B2	27.6(5)	O4-Eu1-B2	142.3(6)
B1-Eu1-B2	89.3(5)	O2-Eu1-B2	103.4(5)
O3-Eu1-B2	90.6(4)	O1-Eu1-B2	28.0(4)
O1-Eu1-B2	94.1(4)	O3-Eu1-B2	76.0(4)

O1-Eu1-B2	150.0(5)	O1-Eu1-B2	86.3(4)
O4-Eu1-B2	142.3(6)	O4-Eu1-B2	27.6(5)
B1-Eu1-B2	89.3(5)	B2-Eu1-B2	120.7(8)
O4-Na1-O4	115.2(11)	O4-Na1-O1	151.1(2)
O4-Na1-O1	72.3(5)	O4-Na1-O1	151.1(2)
O4-Na1-O1	72.3(5)	O1-Na1-O1	57.1(4)
O4-Na1-O1	72.3(5)	O4-Na1-O1	151.1(2)
O1-Na1-O1	115.5(6)	O1-Na1-O1	88.5(5)
O4-Na1-O1	72.3(5)	O4-Na1-O1	151.1(2)
O1-Na1-O1	88.5(5)	O1-Na1-O1	115.5(6)
O1-Na1-O1	57.1(4)	O4-Na1-O2	80.1(4)
O4-Na1-O2	80.1(4)	O1-Na1-O2	73.7(4)
O1-Na1-O2	128.6(4)	O1-Na1-O2	128.6(4)
O1-Na1-O2	73.7(4)	O4-Na1-O2	80.1(4)
O4-Na1-O2	80.1(4)	O1-Na1-O2	128.6(4)
O1-Na1-O2	73.7(4)	O1-Na1-O2	73.7(4)
O1-Na1-O2	128.6(4)	O2-Na1-O2	142.4(13)
O4-Na1-B2	178.6(8)	O4-Na1-B2	66.2(7)
O1-Na1-B2	28.7(2)	O1-Na1-B2	28.7(2)

O1-Na1-B2	106.4(6)	O1-Na1-B2	106.4(6)
O2-Na1-B2	100.3(3)	O2-Na1-B2	100.3(3)
O4-Na1-B2	66.2(7)	O4-Na1-B2	178.6(8)
O1-Na1-B2	106.4(6)	O1-Na1-B2	106.4(6)
O1-Na1-B2	28.7(2)	O1-Na1-B2	28.7(2)
O2-Na1-B2	100.3(3)	O2-Na1-B2	100.3(3)
B2-Na1-B2	112.4(10)	O4-Na1-Na2	108.2(3)
O4-Na1-Na2	108.2(3)	O1-Na1-Na2	45.6(2)
O1-Na1-Na2	94.3(4)	O1-Na1-Na2	94.3(4)
O1-Na1-Na2	45.6(2)	O2-Na1-Na2	54.6(6)
O2-Na1-Na2	163.0(8)	B2-Na1-Na2	71.0(3)
B2-Na1-Na2	71.0(3)	O4-Na1-Na2	108.2(3)
O4-Na1-Na2	108.2(3)	O1-Na1-Na2	94.3(4)
O1-Na1-Na2	45.6(2)	O1-Na1-Na2	45.6(2)
O1-Na1-Na2	94.3(4)	O2-Na1-Na2	163.0(8)
O2-Na1-Na2	54.6(6)	B2-Na1-Na2	71.0(3)
B2-Na1-Na2	71.0(3)	Na2-Na1-Na2	108.5(5)
B1-Rb2-B1	130.8(14)	B1-Rb2-O3	27.1(4)
B1-Rb2-O3	136.4(6)	B1-Rb2-O3	136.4(6)

B1-Rb2-O3	27.1(4)	O3-Rb2-O3	157.1(6)
B1-Rb2-O3	136.4(6)	B1-Rb2-O3	27.1(4)
O3-Rb2-O3	125.2(5)	O3-Rb2-O3	49.0(5)
B1-Rb2-O3	27.1(4)	B1-Rb2-O3	136.4(6)
O3-Rb2-O3	49.0(5)	O3-Rb2-O3	125.2(5)
O3-Rb2-O3	157.1(6)	B1-Rb2-O4	71.9(5)
B1-Rb2-O4	71.9(5)	O3-Rb2-O4	97.3(3)
O3-Rb2-O4	64.9(3)	O3-Rb2-O4	97.3(3)
O3-Rb2-O4	64.9(3)	B1-Rb2-O4	71.9(5)
B1-Rb2-O4	71.9(5)	O3-Rb2-O4	64.9(3)
O3-Rb2-O4	97.3(3)	O3-Rb2-O4	64.9(3)
O3-Rb2-O4	97.3(3)	O4-Rb2-O4	83.4(7)
B1-Rb2-Na2	170.2(7)	B1-Rb2-Na2	59.0(7)
O3-Rb2-Na2	147.7(3)	O3-Rb2-Na2	51.6(3)
O3-Rb2-Na2	51.6(3)	O3-Rb2-Na2	147.7(3)
O4-Rb2-Na2	114.93(19)	O4-Rb2-Na2	114.93(19)
B1-Rb2-Na2	59.0(7)	B1-Rb2-Na2	170.2(7)
O3-Rb2-Na2	51.6(3)	O3-Rb2-Na2	147.7(3)
O3-Rb2-Na2	147.7(3)	O3-Rb2-Na2	51.6(3)

O4-Rb2-Na2	114.93(19)	O4-Rb2-Na2	114.93(19)
Na2-Rb2-Na2	111.3(4)	B1-Rb2-O1	86.8(6)
B1-Rb2-O1	131.0(5)	O3-Rb2-O1	63.8(3)
O3-Rb2-O1	136.7(3)	O3-Rb2-O1	104.7(3)
O3-Rb2-O1	91.9(3)	O4-Rb2-O1	156.74(17)
O4-Rb2-O1	99.1(4)	Na2-Rb2-O1	85.2(3)
Na2-Rb2-O1	43.1(2)	B1-Rb2-O1	131.0(5)
B1-Rb2-O1	86.8(6)	O3-Rb2-O1	104.7(3)
O3-Rb2-O1	91.9(3)	O3-Rb2-O1	63.8(3)
O3-Rb2-O1	136.7(3)	O4-Rb2-O1	156.74(18)
O4-Rb2-O1	99.1(4)	Na2-Rb2-O1	43.1(2)
Na2-Rb2-O1	85.2(3)	O1-Rb2-O1	46.1(3)
O1-Na2-O1	155.3(8)	O1-Na2-O1	72.3(5)
O1-Na2-O1	102.2(5)	O1-Na2-O1	102.2(5)
O1-Na2-O1	72.3(5)	O1-Na2-O1	155.3(8)
O1-Na2-O3	80.4(4)	O1-Na2-O3	123.1(5)
O1-Na2-O3	80.4(4)	O1-Na2-O3	123.1(5)
O1-Na2-O3	123.1(5)	O1-Na2-O3	80.4(4)
O1-Na2-O3	123.1(5)	O1-Na2-O3	80.4(4)

O3-Na2-O3	54.5(6)	O1-Na2-O2	77.7(4)
O1-Na2-O2	77.7(4)	O1-Na2-O2	77.7(4)
O1-Na2-O2	77.7(4)	O3-Na2-O2	152.7(3)
O3-Na2-O2	152.7(3)	O1-Na2-B1	102.3(4)
O1-Na2-B1	102.3(4)	O1-Na2-B1	102.3(4)
O1-Na2-B1	102.3(4)	O3-Na2-B1	27.3(3)
O3-Na2-B1	27.3(3)	O2-Na2-B1	180.0
O1-Na2-Rb2	68.5(3)	O1-Na2-Rb2	127.4(3)
O1-Na2-Rb2	127.4(3)	O1-Na2-Rb2	68.5(3)
O3-Na2-Rb2	59.9(2)	O3-Na2-Rb2	59.9(2)
O2-Na2-Rb2	124.4(2)	B1-Na2-Rb2	55.6(2)
O1-Na2-Rb2	127.4(3)	O1-Na2-Rb2	68.5(3)
O1-Na2-Rb2	68.5(3)	O1-Na2-Rb2	127.4(3)
O3-Na2-Rb2	59.9(2)	O3-Na2-Rb2	59.9(2)
O2-Na2-Rb2	124.4(2)	B1-Na2-Rb2	55.6(2)
Rb2-Na2-Rb2	111.3(4)	O1-Na2-Na1	52.9(3)
O1-Na2-Na1	110.7(4)	O1-Na2-Na1	110.7(4)
O1-Na2-Na1	52.9(3)	O3-Na2-Na1	121.3(2)
O3-Na2-Na1	121.3(2)	O2-Na2-Na1	54.2(2)

B1-Na2-Na1	125.8(2)	Rb2-Na2-Na1	70.14(18)
Rb2-Na2-Na1	178.6(4)	O1-Na2-Na1	110.7(4)
O1-Na2-Na1	52.9(3)	O1-Na2-Na1	52.9(3)
O1-Na2-Na1	110.7(4)	O3-Na2-Na1	121.3(2)
O3-Na2-Na1	121.3(2)	O2-Na2-Na1	54.2(2)
B1-Na2-Na1	125.8(2)	Rb2-Na2-Na1	178.6(4)
Rb2-Na2-Na1	70.14(18)	Na1-Na2-Na1	108.5(5)
B2-O1-Na2	145.9(10)	B2-O1-Eu1	96.3(9)
Na2-O1-Eu1	89.7(4)	B2-O1-Eu1	120.5(10)
Na2-O1-Eu1	92.4(4)	Eu1-O1-Eu1	93.4(3)
B2-O1-Na1	89.7(9)	Na2-O1-Na1	81.5(4)
Eu1-O1-Na1	170.9(5)	Eu1-O1-Na1	89.4(4)
B2-O1-Rb2	77.6(9)	Na2-O1-Rb2	68.4(3)
Eu1-O1-Rb2	96.2(3)	Eu1-O1-Rb2	158.4(4)
Na1-O1-Rb2	78.4(3)	B1-O2-Eu1	94.6(7)
B1-O2-Eu1	94.6(7)	Eu1-O2-Eu1	170.8(13)
B1-O2-Na1	108.8(6)	Eu1-O2-Na1	88.5(3)
Eu1-O2-Na1	88.5(3)	B1-O2-Na1	108.8(6)
Eu1-O2-Na1	88.5(3)	Eu1-O2-Na1	88.5(3)

Na1-O2-Na1	142.4(13)	B1-O2-Na2	180.0
Eu1-O2-Na2	85.4(7)	Eu1-O2-Na2	85.4(7)
Na1-O2-Na2	71.2(6)	Na1-O2-Na2	71.2(6)
B1-O2-Rb2	44.8(3)	Eu1-O2-Rb2	93.2(4)
Eu1-O2-Rb2	93.2(5)	Na1-O2-Rb2	153.6(9)
Na1-O2-Rb2	63.9(4)	Na2-O2-Rb2	135.2(3)
B1-O2-Rb2	44.8(3)	Eu1-O2-Rb2	93.2(4)
Eu1-O2-Rb2	93.2(4)	Na1-O2-Rb2	63.9(4)
Na1-O2-Rb2	153.6(9)	Na2-O2-Rb2	135.2(3)
Rb2-O2-Rb2	89.7(6)	B1-O3-Eu1	172.9(17)
B1-O3-Eu1	91.6(15)	Eu1-O3-Eu1	95.5(5)
B1-O3-Na2	89.4(15)	Eu1-O3-Na2	83.5(5)
Eu1-O3-Na2	179.0(6)	B1-O3-Rb2	73.6(6)
Eu1-O3-Rb2	103.6(3)	Eu1-O3-Rb2	111.8(3)
Na2-O3-Rb2	68.5(3)	B1-O3-Rb2	73.6(6)
Eu1-O3-Rb2	103.6(3)	Eu1-O3-Rb2	111.8(3)
Na2-O3-Rb2	68.5(3)	Rb2-O3-Rb2	125.2(5)
B2-O4-Na1	176.8(16)	B2-O4-Eu1	88.2(5)
Na1-O4-Eu1	91.0(4)	B2-O4-Eu1	88.2(5)

Na1-O4-Eu1	91.0(4)	Eu1-O4-Eu1	149.6(8)
B2-O4-Rb2	102.5(13)	Na1-O4-Rb2	80.7(6)
Eu1-O4-Rb2	105.2(4)	Eu1-O4-Rb2	105.2(4)
O4-B2-O1	118.9(9)	O4-B2-O1	118.9(9)
O1-B2-O1	121.7(16)	O4-B2-Na1	175.4(16)
O1-B2-Na1	61.5(8)	O1-B2-Na1	61.5(8)
O4-B2-Eu1	64.2(5)	O1-B2-Eu1	55.7(6)
O1-B2-Eu1	162.7(13)	Na1-B2-Eu1	116.9(4)
O4-B2-Eu1	64.2(5)	O1-B2-Eu1	162.7(13)
O1-B2-Eu1	55.7(6)	Na1-B2-Eu1	116.9(4)
Eu1-B2-Eu1	120.7(8)	O4-B2-Rb2	111.3(15)
O1-B2-Rb2	76.5(9)	O1-B2-Rb2	76.5(9)
Na1-B2-Rb2	73.4(5)	Eu1-B2-Rb2	86.5(5)
Eu1-B2-Rb2	86.5(5)	O4-B2-Rb2	55.1(11)
O1-B2-Rb2	109.1(9)	O1-B2-Rb2	109.1(9)
Na1-B2-Rb2	120.2(8)	Eu1-B2-Rb2	86.8(4)
Eu1-B2-Rb2	86.8(4)	Rb2-B2-Rb2	166.4(8)
O3-B1-O3	127.(3)	O3-B1-O2	116.6(15)
O3-B1-O2	116.6(15)	O3-B1-Rb2	79.2(8)

O3-B1-Rb2	79.2(8)	O2-B1-Rb2	114.6(7)
O3-B1-Rb2	79.2(8)	O3-B1-Rb2	79.2(8)
O2-B1-Rb2	114.6(7)	Rb2-B1-Rb2	130.8(14)
O3-B1-Eu1	173.(2)	O3-B1-Eu1	60.5(10)
O2-B1-Eu1	56.1(6)	Rb2-B1-Eu1	103.41(15)
Rb2-B1-Eu1	103.41(15)	O3-B1-Eu1	60.5(10)
O3-B1-Eu1	173.(2)	O2-B1-Eu1	56.1(6)
Rb2-B1-Eu1	103.41(15)	Rb2-B1-Eu1	103.41(15)
Eu1-B1-Eu1	112.3(12)	O3-B1-Na2	63.4(15)
O3-B1-Na2	63.4(15)	O2-B1-Na2	180.0
Rb2-B1-Na2	65.4(7)	Rb2-B1-Na2	65.4(7)
Eu1-B1-Na2	123.9(6)	Eu1-B1-Na2	123.9(6)

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

#5 x+1, y+1/2, z-1/2 #6 -x+1, -y+1, z-1 #7 -x, -y+1, z

#8 -x+1, -y+1, z #9 -x+2, -y+1, z #10 -x, -y+1/2, z-1/2

#11 -x+1, -y+1/2, z-1/2 #12 -x+2, -y+1/2, z-1/2 #13 -x+1, -y+1/2, z+1/2

#14 x+1, y, z-1 #15 x, y-1/2, z-1/2 #16 x-1, y, z+1

#17 x-1, y-1/2, z+1/2 #18 x, y-1/2, z+1/2 #19 x, y, z+1

#20 x, y+1/2, z+1/2 #21 -x, -y+1/2, z+1/2 #22 x+1, -y+1/2, z-1/2

#23 x, -y+1/2, z+1/2 #24 x+1, -y+1/2, z+1/2 #25 -x, y, z

#26 -x, y+1/2, z-1/2 #27 -x+1, y+1/2, z-1/2 #28 -x, y+1/2, z+1/2

Figure S1. The EDS spectrum of RNEBO.

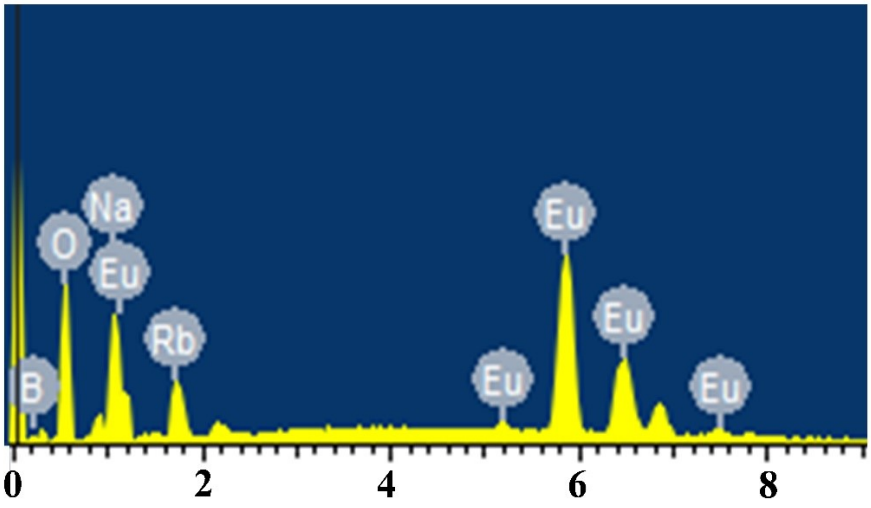

Figure S2. The transition of Eu^{3+} around 400-600 nm in RNEBO.

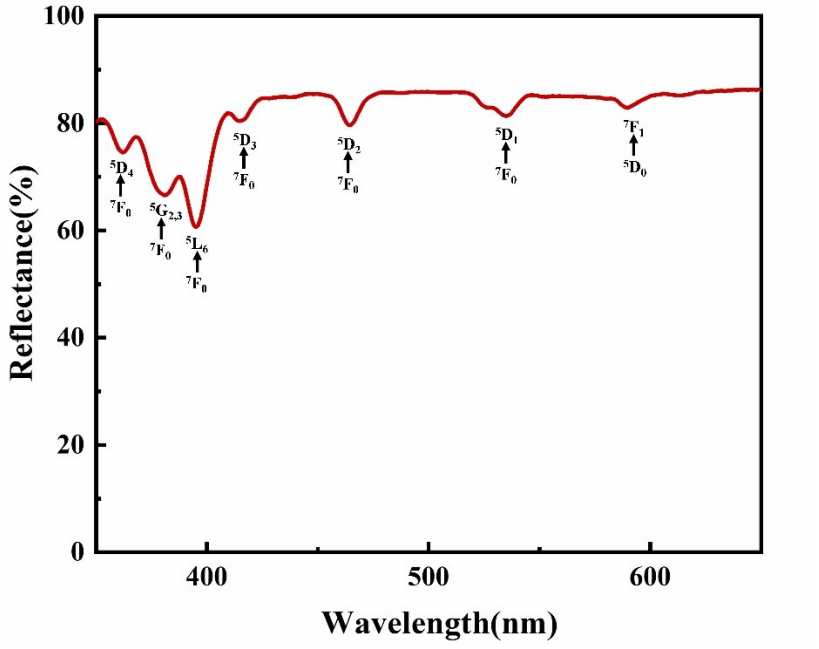

Figure S3. The calculated birefringence for RNEBO.