Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Modulating Optical Performance by Phase Transition in a Nonlinear Optical Material β-$Li_2RbBi(PO_4)_2$

Lei Wu, [a] Ruixin Zhang, [b] Qun Jing, *[b] Hongyu Huang,[a] Xianmeng He,[a] Zhongchang Wang,*[c] Zhaohui Chen*[a]

[a] Key Laboratory of Oil & Gas Fine Chemicals, Ministry of Education and Xinjiang Uyghur Autonomous Region,School of Chemical Engineering and Technology, Xinjiang University, Urumqi 830017, China

[b] Xinjiang Key Laboratory of Solid State Physics and Devices, School of Physical Science and Technology, Xinjiang University, Urumqi 830017, China

[c] International Iberian Nanotechnology Laboratory (INL), Braga 4715-330, Portugal

*To whom correspondence should be addressed. E-mails: chenzhaohui@xju.edu.cn (Z.H.C.); qunjing@xju.edu.cn (Q.J.); zhongchang.wang@inl.int (Z.C.W.)

Contents

Table S1. Crystal data and structure refinements for the β-$Li_2RbBi(PO_4)_2$.

Empirical formula	$Li_2RbBi(PO_4)_2$
Formula weight	498.27
Temperature/K	273(2)
Wavelength/ Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1$
a/Å	8.1067(3)
b/Å	5.0152(2)
c/Å	18.6456(7)
α/°	90.00
β/°	91.0760(10)
γ/°	90.00
Volume/$Å^3$	757.94(5)
Z, Calculated density/ (g/cm^3)	4, 4.376
Absorption coefficient /(mm^{-1})	30.074
F(000)	880.0
Crystal size/mm^3	0.17 × 0.058 × 0.025
2*Θ* range for data collection/°	6.56 to 52
Index ranges	-9 ≤ h ≤ 9, -6 ≤ k ≤ 6, -22 ≤ l ≤ 22
Reflections collected / unique	10992 / 2961 [R(int) = 0.0376]
Completeness to theta = 26.00	99.6 %
Absorption correction	30.074
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2961/73/272
Goodness-of-fit on F^2	1.061
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0353, wR_2 = 0.0962
Final *R* indexes [all data]	R_1 = 0.0374, wR_2 = 0.0974
Extinction coefficient	0.00488(14)
Largest diff. peak/hole / e $Å^{-3}$	2.62/-3.04

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

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for the β-$Li_2RbBi(PO_4)_2$.

Atom	*x*	*y*	*z*	U(eq)
Li(1)	4722(15)	8390(30)	5873(7)	7(1)
Li(2)	11585(16)	13380(30)	7820(7)	10(1)
Li(3)	14532(16)	13440(30)	6938(7)	9(1)
Li(4)	6660(20)	3220(40)	9668(9)	27(4)
Rb(1)	4867(1)	8216(2)	8565(1)	10(1)
Rb(2)	11823(1)	3480(2)	5646(1)	10(1)
Bi(1)	8156(1)	7678(1)	6806(1)	8(1)
Bi(2)	-17(1)	8073(1)	8930(1)	25(1)
P(1)	6876(2)	3346(4)	5680(1)	6(1)
P(2)	7747(3)	3418(4)	8056(1)	10(1)
P(3)	2625(3)	3240(5)	9516(1)	21(1)
P(4)	12206(2)	8415(4)	7078(1)	7(1)
O(1)	13128(8)	8701(13)	5115(3)	15(2)
O(2)	9259(8)	4796(14)	7696(4)	18(2)
O(3)	-2254(10)	4507(16)	8816(4)	30(1)
O(4)	2376(10)	10257(17)	9569(5)	32(2)
O(5)	2594(8)	5484(12)	7137(3)	12(2)
O(6)	7968(10)	461(15)	8062(5)	35(2)
O(7)	6208(9)	4227(16)	7640(4)	27(2)
O(8)	5445(8)	4757(13)	6038(3)	12(1)
O(9)	8521(8)	4628(13)	6000(4)	15(2)
O(10)	1861(11)	4370(17)	8832(5)	38(1)
O(11)	11802(8)	9567(13)	7819(3)	14(2)
O(12)	10655(8)	8823(14)	6587(3)	18(2)
O(13)	6919(7)	300(12)	5858(3)	10(1)
O(14)	13620(8)	9917(12)	6739(3)	11(1)
O(15A)	4120(20)	4550(40)	9816(10)	40(1)
O(15B)	4520(20)	3340(40)	9276(10)	48(1)
O(16A)	2190(20)	4600(30)	10187(9)	30(1)
O(16B)	1000(30)	4760(40)	9974(12)	55(1)

U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S3. Selected bond distances (Å) and angles (deg) for the β-$Li_2RbBi(PO_4)_2$.

Li(1)-O(1)$^{\#1}$	1.903(14)	P(1)-O(1)$^{\#13}$	1.492(6)
Li(1)-O(8)	1.938(15)	P(1)-O(8)	1.525(7)
Li(1)-O(14)$^{\#1}$	2.012(14)	P(1)-O(13)	1.564(6)
Li(1)-O(13)$^{\#2}$	2.023(14)	P(1)-O(9)	1.587(7)
Li(2)-O(5)$^{\#5}$	1.855(15)	P(2)-O(6)	1.494(8)
Li(2)-O(11)	1.920(15)	P(2)-O(7)	1.513(7)
Li(2)-O(10)$^{\#5}$	1.959(16)	P(2)-O(3)$^{\#6}$	1.518(8)
Li(2)-O(2)$^{\#2}$	2.024(15)	P(2)-O(2)	1.570(7)
Li(3)-O(7)$^{\#5}$	1.909(15)	P(3)-O(16A)	1.475(16)
Li(3)-O(5)$^{\#5}$	1.919(15)	P(3)-O(15A)	1.482(18)
Li(3)-O(14)	1.948(15)	P(3)-O(4)$^{\#9}$	1.513(9)
Li(3)-O(8)#5	1.961(15)	P(3)-O(10)	1.517(9)
Li(4)-O(15B)	1.86(2)	P(3)-O(15B)	1.612(18)
Li(4)-O(4)#7	1.907(19)	P(3)-O(16B)	1.76(2)
Li(4)-O(3)#6	1.943(19)	P(4)-O(5)#6	1.507(6)
Li(4)-O(16A)#7	2.06(2)	P(4)-O(14)	1.519(7)
Li(4)-O(15A)	2.18(3)	P(4)-O(11)	1.539(6)
Li(4)-O(15A)#7	2.18(3)	P(4)-O(12)	1.555(6)
Li(4)-O(16B)#7	2.65(3)	O(1)#13-P(1)-O(8)	113.1(4)
Rb(1)-O(15B)	2.80(2)	O(1)#13-P(1)-O(13)	109.1(4)
Rb(1)-O(7)	2.869(8)	O(8)-P(1)-O(13)	112.0(4)
Rb(1)-O(15B)#2	2.91(2)	O(1)#13-P(1)-O(9)	108.1(4)
Rb(1)-O(11)#1	2.905(7)	O(8)-P(1)-O(9)	106.7(4)
Rb(1)-O(6)#2	2.925(9)	O(13)-P(1)-O(9)	107.5(3)
Rb(1)-O(4)	2.962(8)	O(6)-P(2)-O(7)	111.6(5)
Rb(1)-O(3)#6	3.014(8)	O(6)-P(2)-O(3)#6	110.6(5)
Rb(1)-O(15A)	3.039(19)	O(7)-P(2)-O(3)#6	111.6(4)
Rb(1)-O(10)	3.155(9)	O(6)-P(2)-O(2)	110.2(4)
Rb(1)-O(15A)#8	3.184(18)	O(7)-P(2)-O(2)	107.8(4)
Rb(1)-O(16A)#8	3.373(16)	O(3)#6-P(2)-O(2)	104.8(4)
Rb(2)-O(1)#9	2.807(6)	O(16A)-P(3)-O(15A)	71.5(10)

Rb(2)-O(9)	2.828(6)	O(16A)-P(3)-O(4)#9	111.5(7)
Rb(2)-O(1)	2.999(6)	O(15A)-P(3)-O(4)#9	121.5(8)
Rb(2)-O(5)#6	3.012(6)	O(16A)-P(3)-O(10)	116.2(7)
Rb(2)-O(14)#9	3.060(6)	O(15A)-P(3)-O(10)	118.1(8)
Rb(2)-O(8)#6	3.080(6)	O(4)#9-P(3)-O(10)	111.8(5)
Rb(2)-O(12)#9	3.081(7)	O(16A)-P(3)-O(15B)	117.7(9)
Rb(2)-O(13)#10	3.137(6)	O(15A)-P(3)-O(15B)	46.3(10)
Rb(2)-O(12)	3.350(7)	O(4)#9-P(3)-O(15B)	100.3(8)
Bi(1)-O(12)	2.153(6)	O(10)-P(3)-O(15B)	97.6(7)
Bi(1)-O(9)	2.168(7)	O(16A)-P(3)-O(16B)	36.2(9)
Bi(1)-O(2)	2.364(7)	O(15A)-P(3)-O(16B)	103.9(10)
Bi(1)-O(13)#2	2.406(6)	O(4)#9-P(3)-O(16B)	107.2(8)
Bi(1)-O(6)#2	2.734(9)	O(10)-P(3)-O(16B)	87.0(8)
Bi(2)-O(16B)#12	2.36(2)	O(15B)-P(3)-O(16B)	148.1(11)
Bi(2)-O(10)	2.411(9)	O(5)#6-P(4)-O(14)	110.9(4)
Bi(2)-O(4)	2.509(8)	O(5)#6-P(4)-O(11)	110.4(4)
Bi(2)-O(3)	2.553(8)	O(14)-P(4)-O(11)	111.2(4)
Bi(2)-O(16A)#12	2.550(16)	O(5)#6-P(4)-O(12)	109.7(4)
Bi(2)-O(6)#4	2.573(9)	O(14)-P(4)-O(12)	107.3(4)
Bi(2)-O(11)#1	2.673(6)	O(11)-P(4)-O(12)	107.2(4)
Bi(2)-O(16B)	2.68(2)		

Symmetry transformations used to generate equivalent atoms:

#1	x-1, y, z	#2	x, y+1, z	#3	x-1, y-1, z
#4	x-1, y+1, z	#5	x+1, y+1, z	#6	x+1, y, z
#7	-x+1, y-1/2, -z+2	#8	-x+1, y+1/2, -z+2	#9	x, y-1, z
#10	-x+2, y+1/2, -z+1	#11	x+1, y-1, z	#12	-x, y+1/2, -z+2
#13	-x+2, y-1/2, -z+1	#14	-x, y-1/2, -z+2		

Table S4. Anisotropic displacement parameters ($A^2 \times 10^3$) for the β-$Li_2RbBi(PO_4)_2$.

	U11	U22	U33	U23	U13	U12
Li(1)	7(2)	6(2)	7(2)	0(1)	0(1)	0(1)
Li(2)	10(2)	10(2)	10(2)	0(1)	0(1)	0(1)
Li(3)	9(2)	9(2)	9(2)	0(1)	0(1)	0(1)
Li(4)	34(8)	21(9)	24(8)	6(8)	-14(7)	-6(8)
Rb(1)	6(1)	12(1)	12(1)	-1(1)	3(1)	0(1)
Rb(2)	11(1)	10(1)	10(1)	0(1)	3(1)	2(1)
Bi(1)	9(1)	9(1)	6(1)	0(1)	-1(1)	1(1)
Bi(2)	25(1)	24(1)	26(1)	-3(1)	-4(1)	1(1)
P(1)	8(1)	5(1)	5(1)	1(1)	-1(1)	-2(1)
P(2)	10(1)	10(1)	11(1)	4(1)	-1(1)	0(1)
P(3)	25(1)	25(1)	12(1)	2(1)	-4(1)	-16(1)
P(4)	7(1)	5(1)	10(1)	-3(1)	2(1)	-2(1)
O(1)	18(3)	18(3)	9(3)	-8(2)	-5(2)	-3(3)
O(2)	17(3)	22(3)	14(3)	10(3)	-3(3)	-5(3)
O(3)	31(1)	30(1)	28(2)	2(1)	1(1)	1(1)
O(4)	27(4)	38(5)	32(4)	7(4)	-3(4)	-3(4)
O(5)	8(3)	9(3)	17(3)	2(3)	-4(3)	3(2)
O(6)	32(4)	19(4)	53(5)	14(4)	7(4)	2(3)
O(7)	16(3)	39(4)	27(4)	-10(3)	-8(3)	4(3)
O(8)	13(1)	12(1)	13(1)	1(1)	0(1)	2(1)
O(9)	13(1)	11(3)	19(3)	-4(3)	-7(3)	-7(3)
O(10)	40(1)	38(2)	37(2)	0(1)	-1(1)	1(1)
O(11)	21(3)	15(3)	7(3)	-4(2)	6(3)	4(3)
O(12)	13(3)	28(4)	14(3)	8(3)	-4(3)	-3(3)
O(13)	10(1)	10(1)	10(1)	1(1)	-1(1)	0(1)
O(14)	11(1)	10(1)	11(1)	0(1)	0(1)	-1(1)
O(15A)	40(2)	40(2)	40(2)	1(1)	0(1)	0(1)
O(15B)	48(2)	48(2)	49(2)	0(1)	1(1)	0(1)
O(16A)	30(2)	30(2)	29(2)	-1(1)	1(1)	0(1)
O(16B)	55(2)	55(2)	55(2)	0(1)	2(1)	0(1)

Table S5. Bond valence analysis of the β-$Li_2RbBi(PO_4)_2$.

β-$Li_2RbBi(PO_4)_2$								
Atom	Li(1)	Li(2)	Li(3)	Li(4)	Rb(1)	Rb(2)	Bi(1)	Bi(2)
∑ Cations	1.04	1.13	1.13	1.09	1.26	1.19	2.73	2.56
Atom	P(1)	P(2)	P(3)	P(4)	O(1)	O(2)	O(3)	O(4)
∑ Cations	4.76	4.99	4.77	4.90	2.02	1.80	1.95	2.05
Atom	O(5)	O(6)	O(7)	O(8)	O(9)	O(10)	O(11)	O(12)
∑ Cations	2.08	1.96	1.77	1.89	2.07	2.04	1.87	2.15
Atom	O(13)	O(14)	O(15)	O(16)				
∑ Cations	1.86	1.87	1.88	1.79				

Table S6. SHG response of all the Bi-based phosphates.

materials	Group	SHG(× KDP)	ref
$Li_2KBi(PO_4)_2$	$P2_1$	5	1
β-$Li_2RbBi(PO_4)_2$	**$P2_1$**	**5.2**	**this work**
α-$Li_2RbBi(PO_4)_2$	$C2$	3.1	1
$Li_2CsBi(PO_4)_2$	$C2$	2.5	1
$CsBi(P_4O_{12})$	$I\bar{4}3d$	4.2	2
$K_3SrBi(P_2O_7)_2$	$P2_1$	4	3
$Bi_{32}Cd_3P_{10}O_{76}$	$C2$	4	4
$Cd_3Bi(PO_4)_3$	$I\bar{4}3d$	3.8	5
$Pb_3Bi(PO_4)_3$	$I\bar{4}3d$	3	5
$Sr_3Bi(PO_4)_3$	$I\bar{4}3d$	2.85	5
$Rb_3PbBi(P_2O_7)_2$	$P2_1$	2.8	6
$Rb_3BaBi(P_2O_7)_2$	$P2_1$	2.5	7
$Bi_6ZnO_7(PO_4)_2$	$I2$	2.5	8
$Rb_3SrBi(P_2O_7)_2$	$P2_1$	2.1	3
$Cs_3PbBi(P_2O_7)_2$	$P2_12_12_1$	1.1	6
$Cs_3BaBi(P_2O_7)_2$	$P2_12_12_1$	0.8	7
$RbPbBi_2(PO_{4)3}$	$P3_12_1$	0.7	9
$Ca_3Bi(PO_4)_3$	$I\bar{4}3d$	0.64	5
$Ba_3Bi(PO_4)_3$	$I\bar{4}3d$	0.5	10
$K_6Bi_{13}(PO_4)_{15}$	$C2$	weak	11

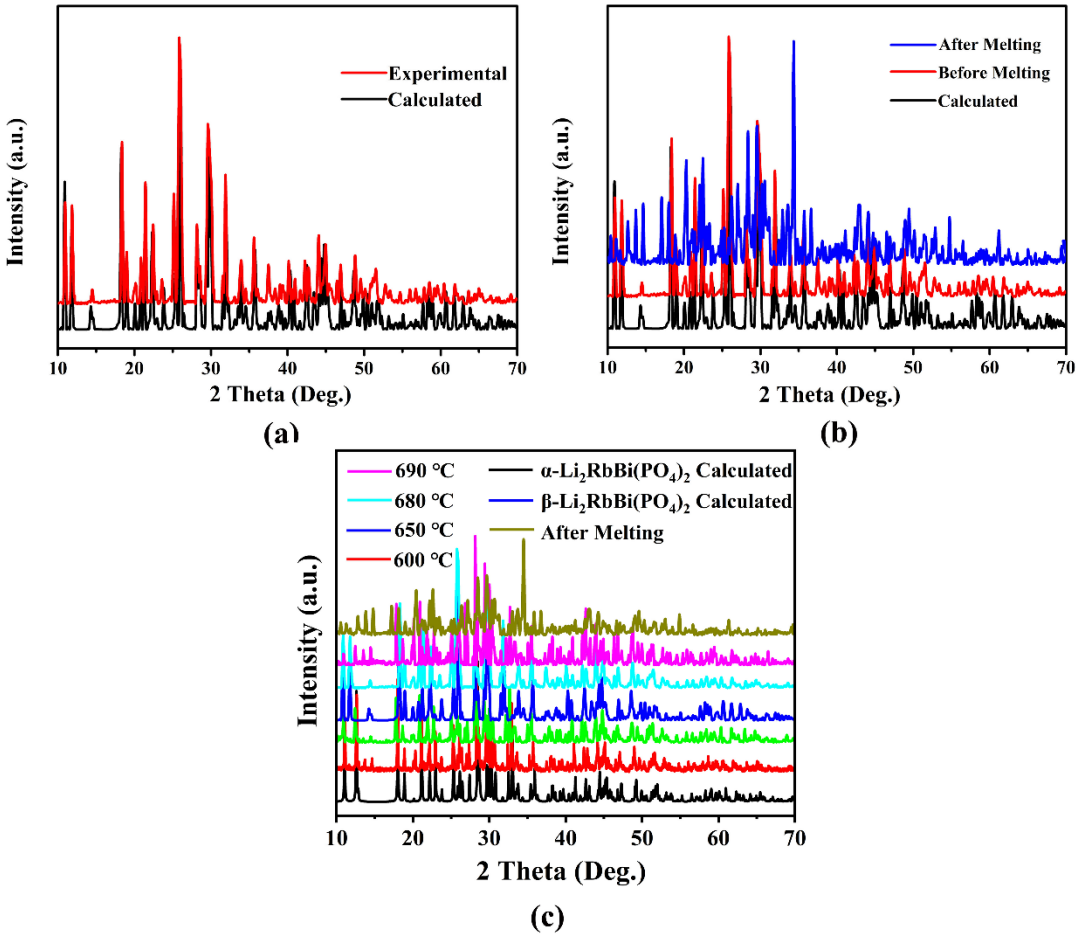

Figure S1. XRD patterns of β-$Li_2RbBi(PO_4)_2$. (a) Experimental and calculated XRD patterns of the β-$Li_2RbBi(PO_4)_2$. (b) XRD patterns of the β-$Li_2RbBi(PO_4)_2$ before and after melting. (c) XRD phase analysis of the sintered samples at different temperatures.

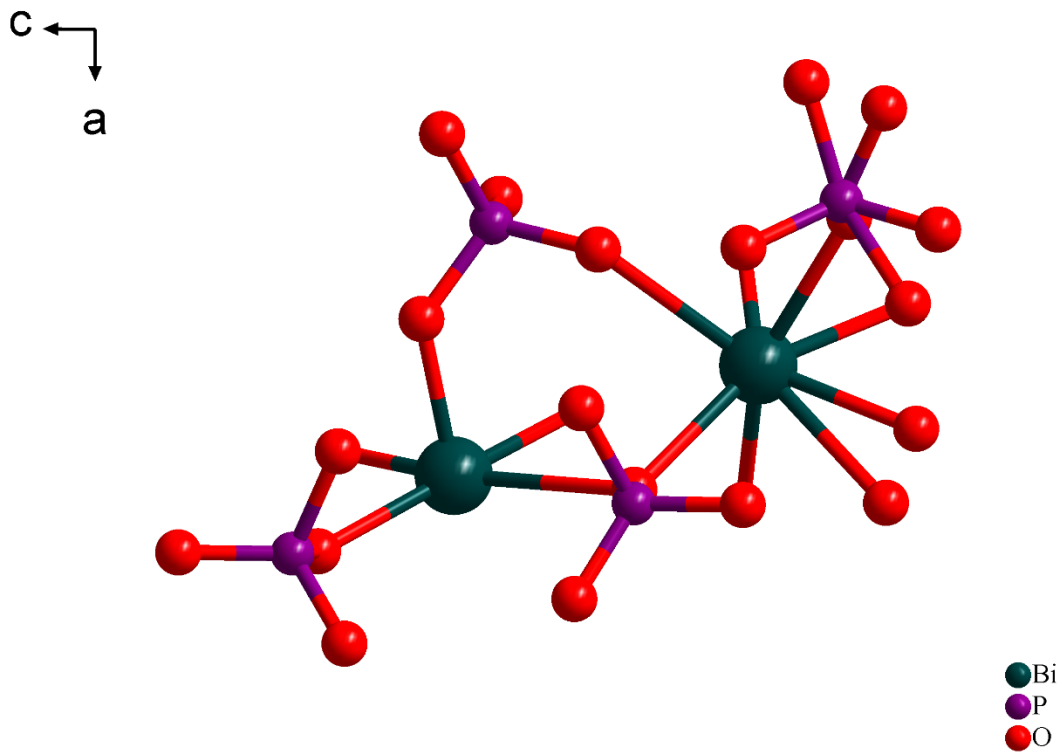

Figure S2. Coordinated environment of Bi atoms in the β-$Li_2RbBi(PO_4)_2$.

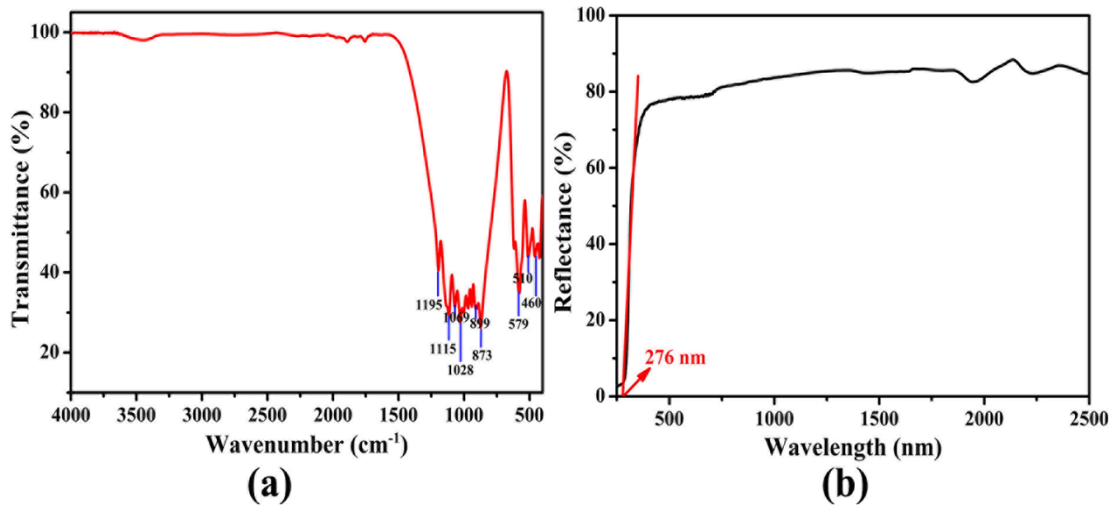

Figure S3. (a,b) IR (a) andUV−Vis−NIR (b) diffuse reflectance spectra of the β-$Li_2RbBi(PO_4)_2$.

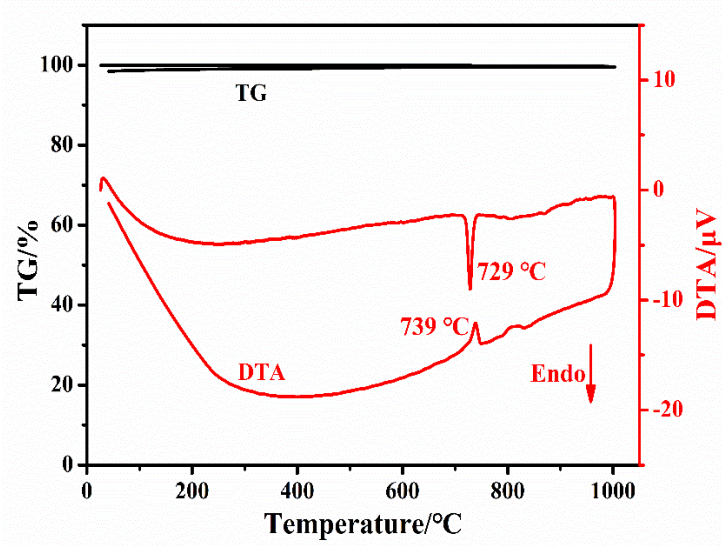

Figure S4. TG-DTA analysis of the β-$Li_2RbBi(PO_4)_2$.

References

1. M. Wen, C. Hu, H. Wu, Z. Yang, H. H. Yu and S. Pan, Three non-centrosymmetric bismuth phosphates, $Li_2ABi(PO_4)_2$(A = K, Rb, and Cs): Effects of Cations on the Crystal Structure and SHG Response, *Inorganic Chemistry Frontiers*, 2020, **7**, 3364-3370.

2. Y. Lian, T. Yu, L. Xiong, L. Wu and L. Chen,Cyclophosphate $MBi(P_4O_{12})$ (M = Cs, Rb): Structure Change Giving Rise to Property Enhancement, *Crystal Growth & Design*, 2020, **20**, 6205-6210.

3. S. Liu, B. Zhang, H. Wu, H. Yu, Z. Hu, J. Wang and Y. Wu, Ultraviolet Nonlinear Optical Crystals $A_3SrBi(P_2O_7)_2$(A = K, Rb) with Large Second Harmonic Generation Responses, *Inorganic Chemistry Frontiers*, 2021, **8**, 2061-2067.

4. J. Wang, B. Xiong, H. Wu, H. Yu, Z. Hu, J. Wang and Y. Wu, $Bi_{32}Cd_3P_{10}O_{76}$: A New Congruently Melting Nonlinear Optical Crystal with a Large SHG Response and a Wide Transparent Region, *Inorganic Chemistry Frontiers*, 2021, **8**, 344-351.

5. P. P. Sahoo and T. N. Guru Row, Crystal Chemistry of the Noncentrosymmetric Eulytites: $A_3Bi(XO_4)_3$ (X = V, A = Pb; X = P, A = Ca, Cd, Sr, Pb), *Inorganic Chemistry*, 2010, **49**, 10013-10021.

6. X. Lu, Z. Chen, X. Shi, Q. Jing and M.-H. Lee, Two Pyrophosphates with Large Birefringences and Second-Harmonic Responses as Ultraviolet Nonlinear Optical Materials, *Angewandte Chemie International Edition*, 2020, **59**, 17648-17656.

7. L. Qi, Z. Chen, X. Shi, X. Zhang, Q. Jing, N. Li, Z. Jiang, B. Zhang and M.-H. Lee, $A_3BBi(P_2O_7)_2$ (A = Rb, Cs; B = Pb, Ba): Isovalent Cation Substitution to Sustain Large Second-Harmonic Generation Responses, *Chemistry of Materials*, 2020, **32**, 8713-8723.

8. J. Olchowka, M. Colmont, A. Aliev, T. T. Tran, P. S. Halasyamani, H. Hagemann and O. Mentré, Original Oxo-centered Bismuth Oxo-arsenates; Critical Effect of PO_4 for AsO_4 Substitution, *CrystEngComm*, 2017, **19**, 936-945.

9. M. Wen, H. Wu, Z. Yang, X. Wu and S. Pan, An Alkali Metal Phosphate $RbPbBi_2(PO_4)_3$ with Three Kinds of Disorder: the Effect of Isolated Soft Cation Units on the Crystal Structure, *Inorganic Chemistry Frontiers*, 2019, **6**, 2050-2054.

10. W. Zhang, X. Lin, H. Zhang, J. Wang, C. Lin, Z. He and W. Cheng, Lone electron-pair enhancement of SHG responses in Eulytite-type Compounds: $AII_3MIII(PO_4)_3$ (A = Pb, M = Bi; A = Ba, M = Bi, La), *Dalton Transactions*, 2010, **39**, 1546-1551.

11. R. Liu, H. Wu, H. Yu, Z. Hu, J. Wang and Y. Wu, $K_6Bi_{13}(PO_4)_{15}$, $K_5Bi(P_2O_7)_2$, $A_5Bi_5(PO_4)_4(P_2O_7)_2$ (A=K, Rb): New Bismuth Phosphates with Different Condensed Phosphate groups, *Journal of Alloys and Compounds*, 2022, **896**, 163066.