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SUPPORTING INFORMATION

$LiRb_2PO_4$: A New Deep-Ultraviolet Nonlinear Optical Phosphate with a Large SHG Response

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CONTENTS

1. Crystal Data

Table S1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $LiRb_2PO_4$. $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	$U_{(eq)}$	BVS
Li1	5000	2056(14)	274(18)	12(3)	1.0785
Rb1	0	1061(1)	-2074(1)	15(1)	0.9727
Rb2	0	4359(1)	-577(1)	16(1)	1.0748
P1	0	1931(2)	2391(2)	8(1)	4.9240
O1	0	1344(5)	4197(8)	12(1)	2.1146
O2	0	3281(5)	2711(7)	14(1)	2.1044
O3	2232(8)	1567(4)	1394(6)	18(1)	2.0606

Table S2. Selected Bond Distances(Å)and Angles (deg) for $LiRb_2PO_4$.

$LiRb_2PO_4$			
Li1-O3	1.866(10)	Rb2-O2	2.825(6)
Li1-O3*1	1.866(10)	Rb2-O1*8	2.928(4)
Li1-O1*2	1.999(17)	Rb2-O1*2	2.928(4)
Li1-O2*2	2.021(16)	Rb2-O2*12	2.988(6)
		Rb2-O3*10	3.005(5)
Rb1-O1*6	2.902(6)	Rb2-O3*2	3.005(5)
Rb1-O1*7	2.906(7)	Rb2-O3*14	3.322(5)
Rb1-O2*2	2.914(4)	Rb2-O3*13	3.322(5)
Rb1-O2*8	2.914(4)		
Rb1-O3	3.020(6)	P1-O3*9	1.530(5)
Rb1-O3*9	3.020(6)	P1-O3	1.530(5)
Rb1-O3*2	3.328(5)	P1-O1	1.548(6)
Rb1-O3*10	3.328(5)	P1-O2	1.553(6)
Rb1-O3*6	3.447(6)		
Rb1-O3*11	3.447(6)	O2-Rb2-O1*8	86.33(12)
		O2-Rb2-O1*2	86.33(12)
O3*1-Li1-O1*2	117.7(5)	O1*8-Rb2-O1*2	147.6(2)
O3-Li1-O2*2	113.6(5)	O2-Rb2-O2*12	142.00(15)
O3*1-Li1-O2*2	113.6(5)	O1*8-Rb2-O2*12	102.57(11)
O1*6-Rb1-O1*7	116.17(14)	O1*2-Rb2-O2*12	102.57(11)
O1*6-Rb1-O2*2	105.09(10)	O2-Rb2-O3*10	123.50(14)
O1*7-Rb1-O2*2	85.13(11)	O1*8-Rb2-O3*10	50.24(15)
O1*6-Rb1-O2*8	105.09(10)	O1*2-Rb2-O3*10	110.81(14)
O1*7-Rb1-O2*8	85.13(11)	O2*12-Rb2-O3*10	88.13(14)
O2*2-Rb1-O2*8	149.6(2)	O2-Rb2-O1*8	86.33(12)
O1*6-Rb1-O3	82.96(15)	O2-Rb2-O1*2	86.33(12)
O1*7-Rb1-O3	149.65(11)	O1*8-Rb2-O1*2	147.6(2)
O2*2-Rb1-O3	66.48(14)	O2-Rb2-O2*12	142.00(15)
O2*8-Rb1-O3	113.77(14)	O1*8-Rb2-O2*12	102.57(11)
		O1*8-Rb2-O3*2	110.81(14)
O3 *9-P1-O3	110.2(4)	O1*2-Rb2-O3*2	50.24(15)
O3*9-P1-O1	109.8(2)	O2*12-Rb2-O3*2	88.13(14)
O3-P1-O1	109.8(2)	O3*10-Rb2-O3*2	62.40(19)
O3 *9-P1-O2	110.3(2)	O1 *8-Rb2-O3 *2	110.81(14)
O3-P1-O2	110.3(2)	O1*2-Rb2-O3 *2	50.24(15)

Symmetry transformations used to generate equivalent atoms:

*1) -x+2, -y+1, z-1/2; *2) x, y, z-1; *3) -x+5/2, -y+3/2, z-1/2; *4) -x+3/2, -y+3/2, z-1/2;

*5) -x+2, y, z; *6) x+1/2,-y+3/2, z-1/2; *7) x, -y+1, z-1/2; *8) -x+2, -y+2, z-1/2;

*9) x+1/2, y+1/2, z; *10) -x+3/2, y+1/2, z; *11) -x+1, y, z.

*1) -x+1, y, z; *2) -x+3/2, -y+3/2, z-1/2; *3) -x+5/2, -y+3/2, z-1/2;

*4) x+1/2, -y+3/2, z-1/2; *5) -x+2, -y+1, z-1/2; *6) -x+2, y, z; *7) -x+2, -y+2, z-1/2; *8) x, y, z-1.

2. PXRD Pattern

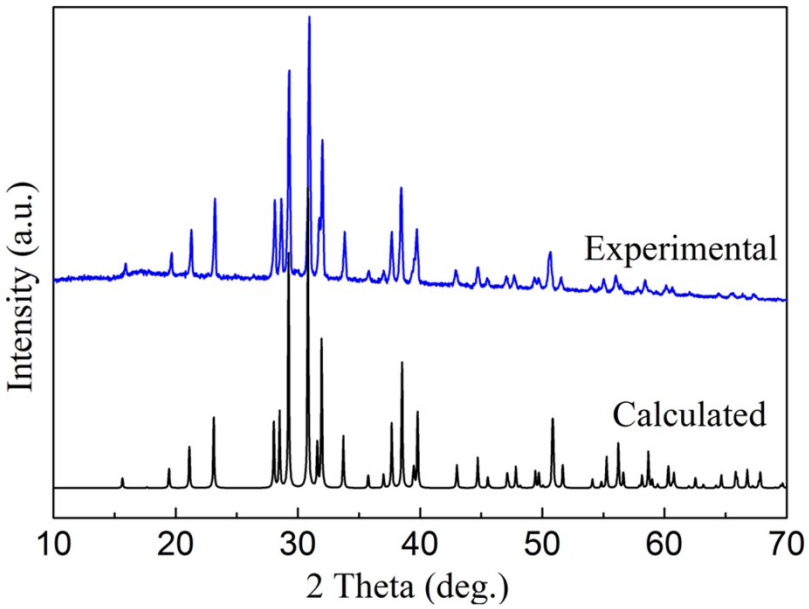

Figure S1. Experimental and calculated XRD patterns for $LiRb_2PO_4$.

3. Crystal Structure

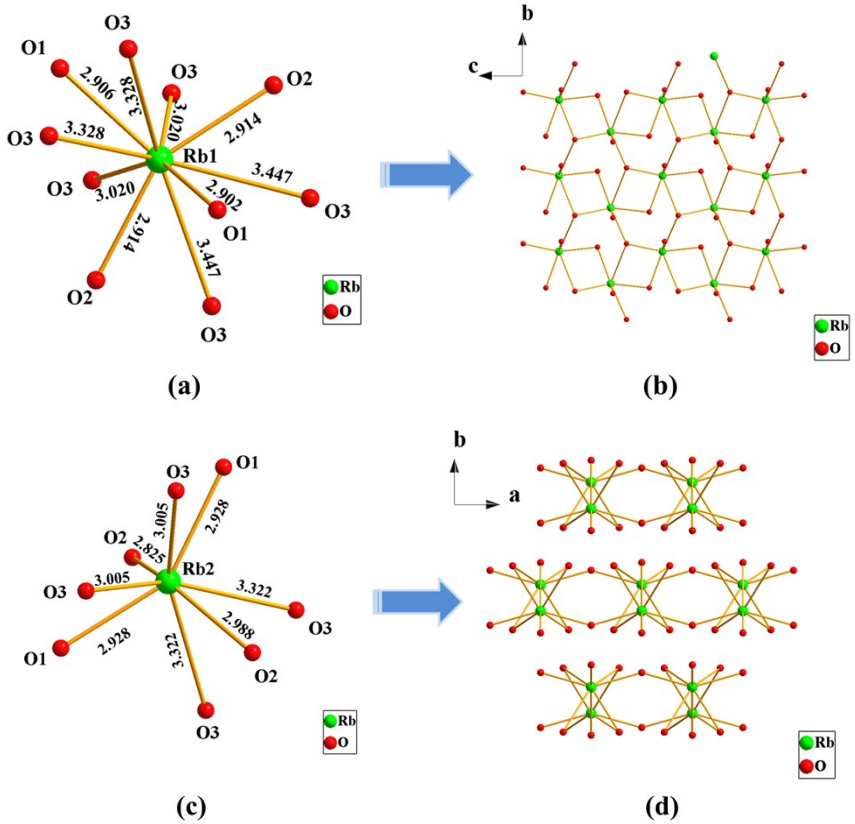

Figure S2. The coordination environments of the Rb1 atoms (a and b); the Rb2 atoms (c and d).

4. IR spectrum

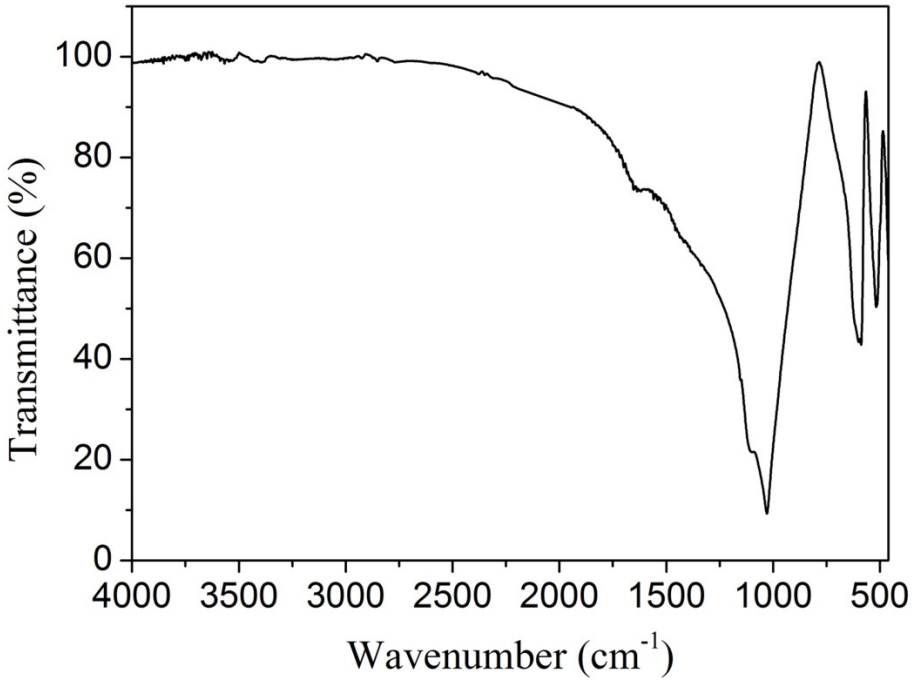

Figure S3. IR spectrum of LRPO.

5. Electronic Structure Calculations

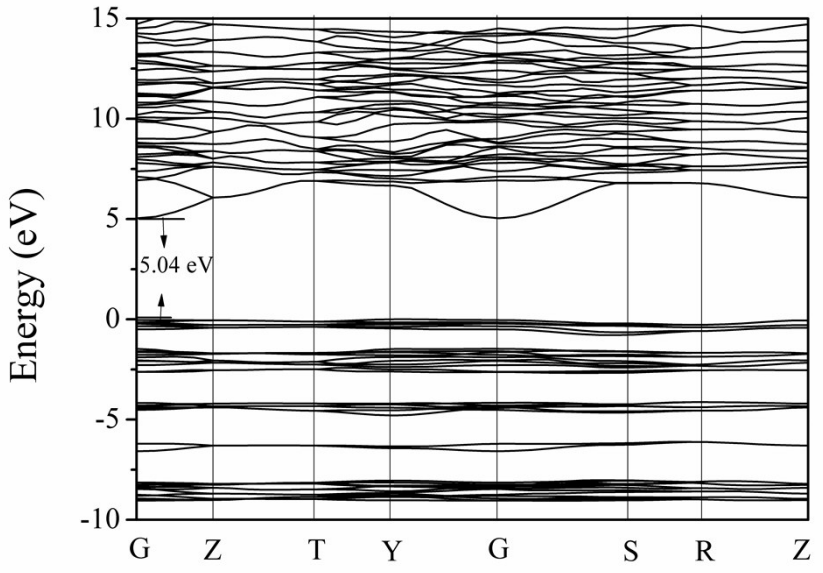

Figure S4. Band structure of LRPO.

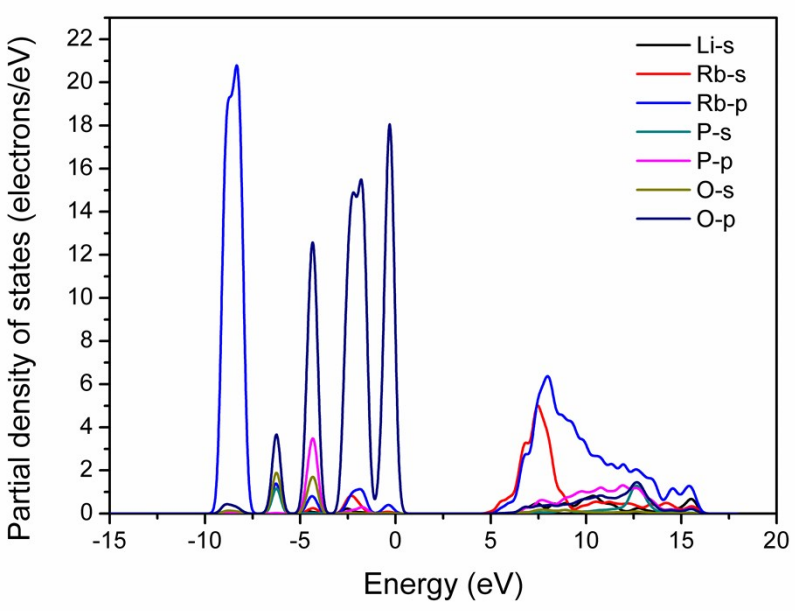

Figure S5. Partial density of states in LRPO.

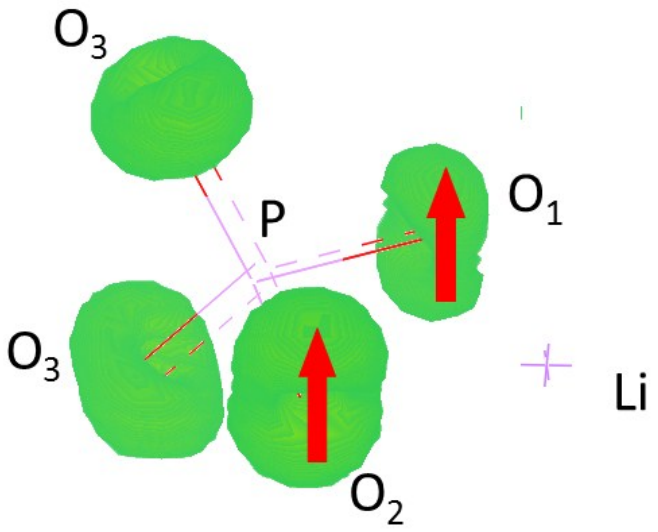

Figure S6. The orientation of the O-2*p* orbital based on orbital analysis

6. Dipole Moments Calculation

Table S3. Calculation of the dipole moments for the PO_4 and LiO_4 and RbO_n (n = 8, 10) polyhedra in LRPO.

	Dipole Moment (Debye)			Total (Debye)
	x/a	*y/b*	*z/c*	
PO_4	0	-0.25	0.88	0.92
	0	-0.25	0.88	0.92
	0	-0.25	0.88	0.92
	0	0.25	0.88	0.92
	0	0.25	0.88	0.92
	0	0.25	0.88	0.92
SUM	0	0.00	5.31	5.31
Net Dipole Moments*			3.54	
	Dipole Moment (Debye)			Total (Debye)
	x/a	*y/b*	*z/c*	
LiO_4	0	-1.24	-4.37	4.54
	0	-1.24	-4.37	4.54
	0	-1.23	-4.37	4.54
	0	1.23	-4.37	4.54
	0	1.23	-4.37	4.54
	0	1.23	-4.37	4.54
SUM	0	0.00	-26.25	26.25
Net Dipole Moments*			17.5	
	Dipole Moment (Debye)			Total (Debye)
	x/a	*y/b*	*z/c*	
$Rb1O_{10}$	0	0.17	-1.14	1.15
	0	0.12	-0.93	0.93
	0	0.12	-0.93	0.93
	0	0.12	-0.93	0.93
	0	-0.12	-0.93	0.93
	0	-0.17	-1.13	0.93
SUM	0	0.25	-5.97	5.97
Net Dipole Moments			3.98	
	Dipole Moment (Debye)			Total (Debye)
	x/a	*y/b*	*z/c*	
$Rb2O_8$	0	-1.92	-1.26	2.3
	0	3.34	-5.14	6.13
	0	1.92	-1.26	2.3
	0	-1.92	-1.26	2.3
	0	-1.92	-1.26	2.3

	0	1.92	-1.26	2.3
SUM	0	0.00	-11.45	11.54
Net Dipole Moments			7.69	

*There are four PO_4 in the crystal cell.

Table S4. Calculation of the dipole moments for the PO_4 polyhedra in LCPO.

	Dipole Moment (Debye)			Total (Debye)
	x/a	*y/b*	*z/c*	
PO_4	0	-0.44	0.95	1.05
	0	-0.44	0.95	1.05
	0	-0.44	0.95	1.05
	0	0.44	0.95	1.05
	0	0.44	0.95	1.05
	0	0.44	0.95	1.05
SUM	0	0.00	5.70	5.70
Net Dipole Moments			3.8	

*There are four PO_4 in the crystal cell.

Table S5. Calculation of the dipole moments for the PO_4 polyhedra in $RbBa_2(PO_3)_5$.

	Dipole Moment (Debye)			Total (Debye)
	x/a	*y/b*	*z/c*	
PO_4	4.23	4.02	2.43	6.32
	4.23	-4.02	2.43	6.32
	-0.29	4.25	0.04	4.26
	-0.29	-4.25	0.04	4.26
	-5.63	2.72	-3.17	7.01
	-5.63	2.72	-3.17	7.01
	2.11	0.88	-2.18	3.96
	2.11	-0.88	-2.18	3.96
	-2.65	-1.99	-2.50	4.15
	-2.65	1.99	-2.50	4.15
SUM	-4.45	5.44	-10.78	12.87
Net Dipole Moments*			12.87	

*There are ten PO_4 in the crystal cell.