Supporting Information

Deep-Ultraviolet Nonlinear-Optical Crystals $LiBePO_4$ and BeP_2O_6 by Ionic Potential Modulation towards Uniform Arrangement of PO_4 Groups

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Table S1 Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (a) $LiBePO_4$ and (b) BeP_2O_6. *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

(a) $LiBePO_4$

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq)	BVS
Li1	3550(4)	8010(4)	4712(3)	18.8(8)	0.87
Li2	5972(3)	574(4)	4711(3)	21.2(10)	0.81
Li3	5740(3)	5297(4)	4773(3)	15.8(8)	0.88
Li4	6134(3)	1757(4)	7247(3)	14.5(8)	0.96
Li5	3160(3)	12849(4)	4741(3)	16.0(8)	0.88
Li6	3639(3)	−767(4)	7250(3)	14.3(8)	0.97
Li7	6412(3)	7020(4)	7251(3)	13.8(8)	0.98
Li8	8918(3)	−483(4)	7256(3)	16.0(8)	0.96
Be1	2888.8(18)	5611(3)	5375.6(18)	7.7(5)	2.07
Be2	5441.2(18)	629(3)	2819.5(19)	7.1(5)	2.08
Be3	5414.6(18)	−1901(3)	5368.2(19)	7.0(5)	2.07
Be4	2931.4(19)	3114(3)	2832.2(19)	7.9(5)	2.11
Be5	5087.2(19)	2806(3)	5351.2(19)	7.3(5)	2.08
Be6	2625.4(19)	10273(3)	5350.0(18)	7.1(5)	2.04
Be7	5721.0(18)	5337(3)	2847.9(19)	6.9(5)	2.09
Be8	3226.5(18)	7853(3)	2833.7(19)	7.1(5)	2.09
P1	4470.4(3)	321.5(6)	5970.0(3)	4.65(12)	5.32

P2	1955.5(3)	7836.8(6)	5972.0(3)	4.60(12)	5.35
P3	4760.6(3)	5644.0(6)	5977.8(3)	4.64(12)	5.31
P4	5107.6(3)	7832.5(6)	3473.0(3)	4.27(12)	5.33
P5	7272.7(3)	−1876.7(6)	5971.4(3)	4.50(12)	5.28
P6	4817.5(3)	3085.6(6)	3461.8(3)	4.37(12)	5.27
P7	2591.9(3)	10310.0(6)	3472.2(3)	4.34(11)	5.23
P8	2330.4(3)	5604.7(6)	3466.8(3)	4.37(12)	5.40
O1	1081.1(9)	7456.1(15)	6082.1(9)	7.7(3)	2.00
O2	5466.5(9)	6831.8(15)	6106.2(9)	7.6(3)	2.03
O3	3845.5(9)	6356.4(15)	5607.5(9)	7.4(3)	2.00
O4	6363.5(9)	−1144.9(15)	5608.2(9)	7.6(3)	1.99
O5	2797.1(10)	11946.3(15)	3547.5(10)	8.1(3)	2.03
O6	2265.4(10)	4451.1(14)	2747.1(9)	7.3(3)	2.00
O7	3251.6(10)	9545.6(14)	3131.6(9)	7.4(3)	1.95
O8	4368.3(10)	1878.4(14)	5591.3(9)	7.4(3)	1.97
O9	2704.0(10)	7763.7(16)	6892.1(9)	8.0(3)	2.06
O10	3609.0(9)	−86.7(15)	6099.3(9)	7.4(3)	2.01
O11	4768.9(10)	1951.2(14)	2736.0(9)	7.4(3)	2.01
O12	5754.7(9)	7040.4(14)	3129.5(9)	7.4(3)	1.96
O13	2571.0(11)	4835.3(13)	4382.1(10)	7.4(3)	1.95
O14	7358.5(11)	−3008.2(15)	5297.2(10)	8.5(3)	2.00
O15	5228.7(10)	248.9(15)	6886.3(9)	7.9(3)	2.07

O16	5485.6(10)	4317.2(15)	3564.6(10)	8.2(3)	1.98
O17	5083.3(11)	2305.8(14)	4371.7(10)	8.2(3)	1.97
O18	7982.6(9)	−698.4(14)	6098.6(9)	7.6(3)	2.03
O19	4643.4(10)	−743.9(15)	5306.9(10)	8.2(3)	1.97
O20	5183.0(11)	7254.8(15)	4401.8(10)	7.9(3)	1.98
O21	1661.8(9)	9948.0(14)	2800.0(9)	7.6(3)	2.03
O22	5337.2(10)	9460.2(15)	3556.7(10)	8.0(3)	1.98
O23	1885.1(10)	9382.8(14)	5583.0(9)	7.0(3)	2.02
O24	1419.5(9)	6346.8(14)	3165.4(9)	8.3(3)	1.93
O25	2709.0(10)	9730.7(14)	4407.9(10)	7.7(3)	1.99
O26	3903.6(9)	3806.1(14)	3159.6(9)	8.2(3)	1.96
O27	3013.7(10)	6804.2(16)	3560.1(10)	8.4(3)	1.96
O28	4850.8(10)	4523.7(15)	5301.9(10)	8.8(3)	1.99
O29	7419.6(10)	−2589.0(16)	6879.1(10)	8.2(3)	2.05
O30	2117.2(10)	6745.6(15)	5321.0(10)	8.9(3)	1.99
O31	4910.8(10)	4928.4(16)	6885.9(9)	8.3(3)	2.05
O32	4174.2(9)	7493.5(14)	2794.1(9)	8.2(3)	2.00

(b) BeP_2O_6

Atom	x/a	y/b	z/c	U(eq)	BVS
Be1	6779(7)	388(7)	6830(4)	15.5(10)	2.21
Be2	6770(7)	601(6)	1799(4)	12.0(10)	2.22
Be3	−1171(7)	4990(7)	5820(4)	15.5(11)	2.20
Be4	1429(7)	10018(6)	9147(4)	14.6(10)	2.20
P1	6133.8(14)	3024.3(13)	3273.8(7)	12.1(2)	5.32
P2	5902.1(14)	2531.5(15)	5353.0(7)	18.0(3)	5.35
P3	1744.6(14)	2667.1(12)	5552.6(7)	13.0(2)	5.31
P4	988.3(14)	375.7(13)	7072.1(7)	12.6(3)	5.33
P5	6011.5(14)	2992.0(13)	8205.6(7)	12.5(2)	5.28
P6	9147.5(14)	5161.3(13)	7965.9(7)	12.5(3)	5.27
P7	8501.1(14)	7514.4(13)	9418.5(7)	12.5(2)	5.23
P8	4401.9(14)	7795.4(13)	9716.2(7)	13.8(2)	5.40
O1	6872(5)	1850(4)	2623(3)	32.5(9)	2.04
O2	4417(5)	3834(4)	2970(3)	32.1(9)	2.08
O3	7795(4)	4195(4)	3521(2)	23.6(7)	2.06
O4	5850(5)	2215(5)	4256(2)	31.5(9)	2.09
O5	7138(6)	3816(5)	5595(3)	46.6(13)	2.10
O6	6220(6)	983(5)	5784(2)	37.2(10)	2.10
O7	3884(5)	3113(5)	5579(3)	35.6(9)	2.13
O8	1357(6)	1538(4)	4801(2)	30.5(8)	2.22

O9	748(5)	4163(4)	5523(2)	28.1(8)	2.11
O10	1456(6)	1966(4)	6572(2)	33.9(9)	2.02
O11	−1002(5)	−17(5)	6919(3)	29.1(8)	2.11
O12	1738(4)	506(4)	8053(2)	19.6(6)	2.18
O13	6133(5)	1678(4)	7550(2)	29.5(8)	2.10
O14	4640(4)	4207(4)	7956(3)	26.6(8)	2.08
O15	8056(4)	3692(4)	8346(3)	27.8(8)	2.15
O16	8790(5)	5387(4)	6943(2)	21.9(7)	2.20
O17	8104(5)	6532(4)	8488(2)	27.1(8)	2.09
O18	11095(4)	4960(4)	8334(2)	19.1(7)	2.19
O19	9764(5)	8781(4)	9187(3)	28.5(8)	2.02
O20	9049(5)	6509(4)	10224(2)	25.4(7)	2.21
O21	6517(4)	8272(4)	9570(3)	24.1(7)	2.27
O22	5623(5)	2283(4)	9210(2)	28.6(8)	2.15
O23	3936(5)	6382(4)	9177(2)	26.0(8)	2.22
O24	3321(4)	9237(4)	9583(2)	24.1(7)	2.06

Table S2 Selected bond distances (Å) and angles (deg) for (a) $LiBePO_4$ and (b) BeP_2O_6.

(a) $LiBePO_4$

Atom–Atom	Length/Å	Atom–Atom	Length/Å
P1–O8	1.532(1)	Be5–O1	1.644(3)
P1–O10	1.541(2)	Be5–O17	1.627(3)
P1–O15	1.530(2)	Be5–O28	1.613(3)
P1–O19	1.540(2)	Be5–O8	1.606(3)
P2–O1	1.541(2)	Be6–O10$^{\#3}$	1.644(3)
P2–O9	1.527(2)	Be6–O14$^{\#13}$	1.626(3)
P2–O23	1.532(1)	Be6–O23	1.611(3)
P2–O30	1.532(2)	Be6–O25	1.637(3)
P3–O2	1.542(2)	Be7–O21$^{\#11}$	1.606(3)
P3–O3	1.535(1)	Be7–O31$^{\#4}$	1.634(3)
P3–O28	1.534(1)	Be7–O12	1.618(3)
P3–O31	1.526(2)	Be7–O16	1.628(3)
P4–O12	1.539(1)	Be8–O29$^{\#5}$	1.624(3)
P4–O20	1.535(2)	Be8–O27	1.638(3)
P4–O22	1.529(1)	Be8–O28	1.624(3)
P4–O32	1.541(1)	Be8–O32	1.606(3)
P5–O4	1.534(1)	Li1–O19$^{\#3}$	2.035(5)
P5–O14	1.536(2)	Li1–O25	2.028(4)
P5–O18	1.541(1)	Li1–O27	2.045(5)
P5–O29	1.525(2)	Li1–O3	2.014(4)
P6–O11	1.535(1)	Li2–O22$^{\#1}$	2.025(5)
P6–O16	1.534(2)	Li2–O30$^{\#11}$	2.062(5)
P6–O17	1.530(2)	Li2–O17	2.081(5)
P6–O26	1.537(2)	Li2–O4	2.065(4)

P7–O5	1.529(1)	Li3–O23$^{\#11}$	2.022(4)
P7–O7	1.542(2)	Li3–O16	2.027(4)
P7–O21	1.538(1)	Li3–O20	1.997(4)
P7–O25	1.529(2)	Li3–O28	2.056(5)
P8–O6	1.535(1)	Li4–O1$^{\#11}$	1.938(4)
P8–O13	1.537(2)	Li4–O6$^{\#12}$	2.047(4)
P8–O24	1.542(2)	Li4–O12$^{\#9}$	2.056(4)
P8–O27	1.533(2)	Li4–O15	1.947(4)
Be1$^{\#11}$–O18	1.631(3)	Li5–O8$^{\#3}$	2.134(5)
Be1–O13	1.638(3)	Li5–O13$^{\#3}$	2.037(4)
Be1–O30	1.610(3)	Li5–O14$^{\#13}$	1.993(5)
Be1–O30	1.618(3)	Li5–O18$^{\#13}$	2.648(4)
Be2–O15$^{\#7}$	1.614(3)	Li6–O10	1.924(4)
Be2–O22$^{\#1}$	1.645(3)	Li6–O7$^{\#9}$	2.070(4)
Be2–O24$^{\#11}$	1.624(3)	Li6–O9$^{\#1}$	1.956(4)
Be2–O11	1.606(3)	Li6–O11$^{\#10}$	2.031(4)
Be3–O2	1.633(3)	Li7–O2	1.917(4)
Be3–O4	1.609(3)	Li7–O29$^{\#3}$	1.977(4)
Be3–O19	1.620(3)	Li7–O21$^{\#14}$	1.978(4)
Be3–O20	1.640(3)	Li7–O24$^{\#14}$	2.086(4)
Be4–O6	1.609(3)	Li8–O18	1.925(5)
Be4–O5$^{\#1}$	1.637(3)	Li8–O26$^{\#12}$	2.112(4)
Be4–O9$^{\#4}$	1.620(3)	Li8–O31$^{\#11}$	1.956(4)
Be4–O26	1.607(3)	Li8–O32$^{\#12}$	2.009(4)

Atom−Atom−Atom	Angle/deg	Atom−Atom−Atom	Angle/deg
O8−P1−O10	107.83(8)	O15−P1−O8	110.45(8)
O15−P1−O10	108.57(8)	O29−P5−O14	110.76(8)

O15−P1−O19	109.93(9)	O29−P5−O18	109.06(8)
O9−P2−O1	109.09(8)	O11−P6−O26	106.18(8)
O9−P2−O23	110.13(8)	O16−P6−O11	114.46(8)
O9−P2−O30	110.3(9)	O16−P6−O26	106.75(8)
O23−P2−O1	108.7(8)	O17−P6−O11	108.58(8)
O23−P2−O30	109.43(8)	O17−P6−O16	107.4(9)
O30−P2−O1	109.17(8)	O17−P6−O26	113.62(9)
O3−P3−O2	109.01(8)	O5−P7−O7	108.09(8)
O28−P3−O2	107.67(8)	O5−P7−O21	113.39(8)
O28−P3−O3	110.18(8)	O21−P7−O7	107.14(8)
O31−P3−O3	109.94(9)	O25−P7−O5	108.53(8)
O4−P5−O18	108.7(8)	O25−P7−O7	109.57(8)
O29−P5−O4	109.7(8)		

Symmetry transformations used to generate equivalent atoms:
$^{\#1}$ +X, −1+Y, +Z; $^{\#2}$ −1/2+X, 1/2+Y, +Z; $^{\#3}$ +X, 1+Y, +Z; $^{\#4}$ +X, 1−Y, −1/2+Z; $^{\#5}$ −1/2+X, 1/2−Y, −1/2+Z; $^{\#6}$ 1/2+X, −3/2+Y, +Z; $^{\#7}$ +X, −Y, −1/2+Z; $^{\#8}$ −1/2+X, 3/2−Y, −1/2+Z; $^{\#9}$ +X, 1−Y, 1/2+Z; $^{\#10}$ +X, −Y, 1/2+Z; $^{\#11}$ 1/2+X, −1/2+Y, +Z; $^{\#12}$ 1/2+X, 1/2−Y, 1/2+Z

(b) BeP_2O_6

Atom−Atom	Length/Å	Atom−Atom	Length/Å
P1–O3	1.568(3)	P6–O17	1.597(3)
P1–O2	1.440(3)	P7–O21	1.577(3)
P1–O1	1.483(4)	P7–O19	1.460(3)
P1–O4	1.575(3)	P7–O17	1.567(3)
P2–O4	1.567(3)	P7–O20	1.457(3)
P2–O7	1.568(3)	P8–O24	1.461(4)

P2–O5	1.434(4)	P8–O23	1.457(4)
P2–O6	1.472(4)	P8–O21	1.581(3)
P3–O9	1.465(4)	P8–O22$^{\#1}$	1.578(3)
P3–O10	1.584(4)	Be1–O2	1.616(6)
P3–O8	1.448(3)	Be1–O11$^{\#4}$	1.606(6)
P3–O7	1.561(3)	Be1–O13	1.592(6)
P4–O12	1.449(3)	Be1–O22	1.616(7)
P4–O11	1.451(3)	Be2–O18$^{\#10}$	1.633(6)
P4–O32	1.603(3)	Be2–O14$^{\#2}$	1.612(6)
P4–O10	1.583(4)	Be2–O23$^{\#2}$	1.580(6)
P5–O14	1.452(4)	Be2–O1	1.579(6)
P5–O15	1.568(3)	Be3–O16$^{\#7}$	1.622(6)
P5–O13	1.465(4)	Be3–O8$^{\#12}$	1.592(6)
P5–O22	1.582(3)	Be3–O5$^{\#7}$	1.580(6)
P6–O18	1.450(3)	Be3–O9	1.615(6)
P6–O16	1.458(3)	Be4–O12$^{\#11}$	1.627(6)
P6–O15	1.592(3)	Be4–O19$^{\#7}$	1.591(6)

Atom−Atom−Atom	Angle/deg	Atom−Atom−Atom	Angle/deg
O3–P1–O4	103.2(2)	O19–P7–O21	106.8(2)
O2–P1–O3	111.2(2)	O14–P5–O15	110.6(2)
O2–P1–O1	118.2(2)	O14–P5–O13	118.0(2)
O2–P1–O4	108.5(2)	O14–P5–O22	109.7(2)
O1–P1–O3	106.3(2)	O15–P5–O22	104.5(2)
O1–P1–O4	108.5(2)	O13–P5–O15	106.3(2)
O4–P2–O7	107.3(2)	O13–P5–O22	106.8(2)
O5–P2–O4	109.8(2)	O18–P6–O16	117.6(2)
O5–P2–O7	104.9(2)	O18–P6–O15	104.9(2)

O5–P2–O6	121.6(3)	O18–P6–O17	112.4(2)
O6–P2–O4	104.0(2)	O16–P6–O15	112.6(2)
O6–P2–O7	108.6(2)	O16–P6–O17	107.7(2)
O9–P3–O10	105.4(2)	O15–P6–O17	100.2(2)
O9–P3–O7	104.5(2)	O19–P7–O17	106.9(2)
O8–P3–O9	120.0(2)	O17–P7–O21	103.0(2)
O8–P3–O10	112.3(2)	O20–P7–O21	109.3(2)
O8–P3–O7	108.4(2)	O20–P7–O19	118.8(2)
O7–P3–O10	105.0(2)	O20–P7–O17	110.8(2)
O12–P4–O11	116.5(2)	O24–P8–O21	104.9(2)
O12–P4–O3	111.8(2)	O24–P8–O22$^{\#1}$	108.5(2)
O12–P4–O10	106.5(2)	O23–P8–O24	122.8(2)
O11–P4–O3	109.1(2)	O23–P8–O21	109.3(2)
O11–P4–O10	111.5(2)	O23–P8–O22$^{\#1}$	104.5(2)
O10–P4–O3	100.2(2)	O22$^{\#1}$–P8–O21	105.8(2)

Symmetry transformations used to generate equivalent atoms:
$^{\#1}$ −X, 1/2+Y, 2−Z; $^{\#2}$ 1−X, −1/2+Y, 1−Z; $^{\#3}$ 2−X, 1/2+Y, 1−Z; $^{\#4}$ 1+X, +Y, +Z; $^{\#5}$ +X, −1+Y, +Z; $^{\#6}$ 1−X, 1/2+Y, 1−Z; $^{\#7}$ −1+X, +Y, +Z; $^{\#8}$ 1−X, −1/2+Y, 2−Z; $^{\#9}$ −X, −1/2+Y, 1−Z; $^{\#10}$ 2−X, −1/2+Y, 1−Z; $^{\#11}$ +X, 1+Y, +Z; $^{\#12}$ −X, 1/2+Y, 1−Z

Table S3 Applicability of ionic potential modulation strategy in known alkali/alkaline-earth metal NLO materials.

Compound	Ions	φ	SHG	Ref.
α-$KZnPO_4$	K^+	6.45	0.2 × KDP	1
α-$LiZnPO_4$	Li^+	16.95	2.9 × KDP	1
$K_2SrP_4O_{12}$	Sr^{2+}	15.87	0.5 × KDP	2
$KMg(H_2O)PO_4$	Mg^{2+}	27.78	1.14 × KDP	3
$Ba_3P_3O_{10}Cl$	Ba^{2+}	14.08	0.6 × KDP	4
Mg_2PO_4Cl	Mg^{2+}	27.78	5.2 × KDP	5
Na_2BeSiO_4	Na^+	8.85	0.6 × KDP	6
Li_2BeSiO_4	Li^+	16.95	1.6 × KDP	6
$Li_{2.9}Cs_{1.1}(SO_4)_2$	Cs^+	5.52	0.3 × KDP	7
$LiKSO_4$	K^+	7.25	1.2 × KDP	8
$Li_4Cs_3B_7O_{14}$	Cs^+	5.62	0.5 × KDP	9
$Li_4Sr(BO_3)_2$	Sr^{2+}	15.87	2.0 × KDP	10
$CsZn_2B_3O_7$	Cs^+	5.52	1.6 × KDP	11
$Ba_5Zn_4(BO_3)_6$	Ba^{2+}	14.08	2.5 × KDP	12
$KNa_4B_2P_3O_{13}$	K^+	6.62	0.4 × KDP	13
$Na_5B_2P_3O_{13}$	Na^+	8.62	1.0 × KDP	14
$CsBPO_4F$	Cs^+	5.32	0.3 × KDP	15
$KBPO_4F$	K^+	6.45	1.1 × KDP	15
$RbCaCO_3F$	Rb^+	5.92	1.11 × KDP	16
$KCaCO_3F$	K^+	7.25	3.61 × KDP	16
$RbCaCO_3F$	Ca^{2+}	18.19	1.11 × KDP	16
$RbMgCO_3F$	Mg^{2+}	35.09	4.0 × KDP	17
$RbCd_4Ga_3S_9$	Rb^+	5.82	0.01 × AGS	18
$KCd_4Ga_5S_{12}$	K^+	6.45	2.0 × AGS	19
$Na_2Hg_3Sn_2Se_8$	Na^+	8.85	5.4 × AGS	20
$Li_2HgSnSe_4$	Li^+	16.95	6.0 × AGS	20

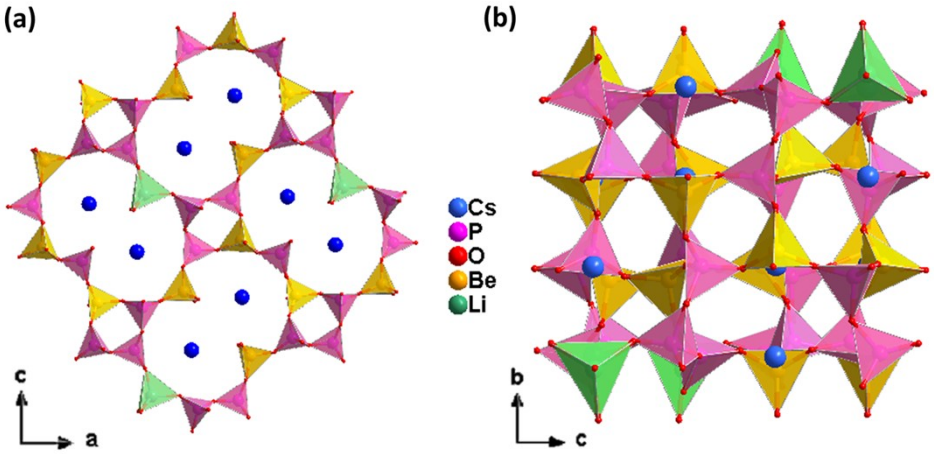


Fig. S1 Crystal structure of $Cs_4LiBe_4P_7O_{24}$. (a) $[LiBe_4P_7O_{24}]_\infty$ pseudo layers with twelve-membered rings. (b) 3D stacking of $[LiBe_4P_7O_{24}]_\infty$ pseudo layers viewed along the *a*-axis.

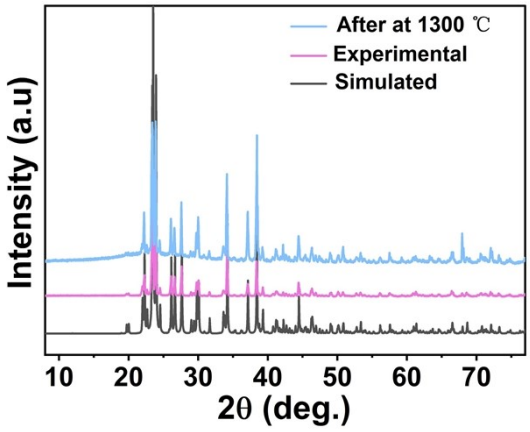


Fig. S2 Powder XRD patterns of $LiBePO_4$ before and after melting.

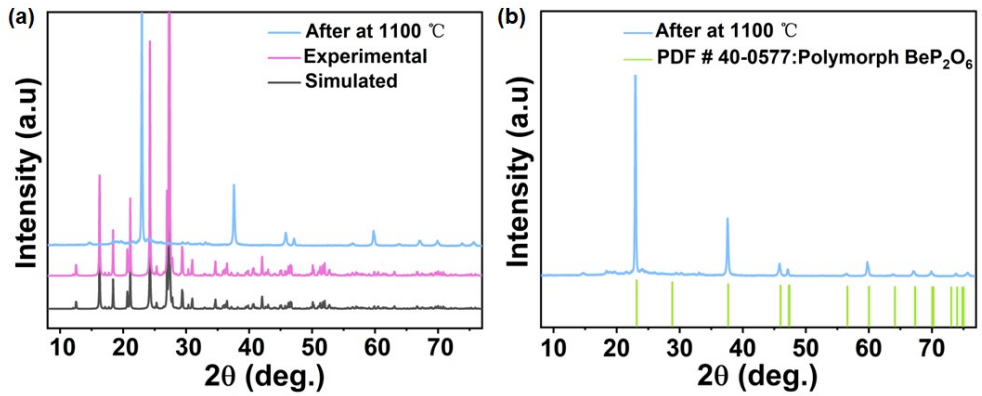
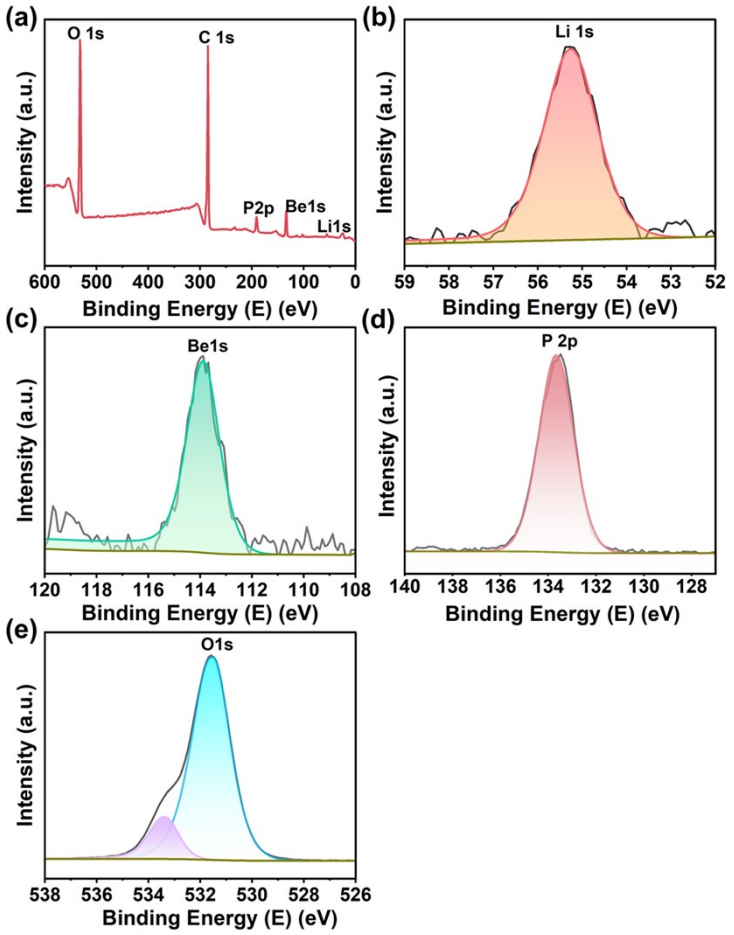
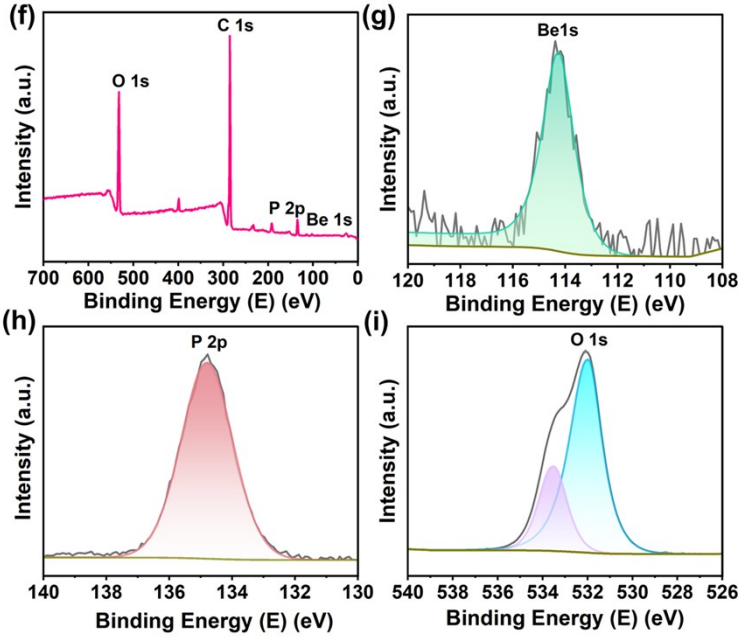


Fig. S3 (a) Powder XRD patterns of BeP_2O_6 before and after melting BeP_2O_6. (b) Powder XRD patterns of BeP_2O_6 after melting.



(a) $LiBePO_4$



(b) BeP_2O_6

Fig. S4 XPS spectra of (a) $LiBePO_4$ and (b) BeP_2O_6. $LiBePO_4$: (a) XPS survey scan. (b)-(e) Fine XPS spectra of Li1s, Be 1s, P 2p, and O 1s, respectively. BeP_2O_6: (f) XPS survey scan. (g)-(i) Fine XPS spectra of Be 1s, P 2p, and O 1s, respectively.

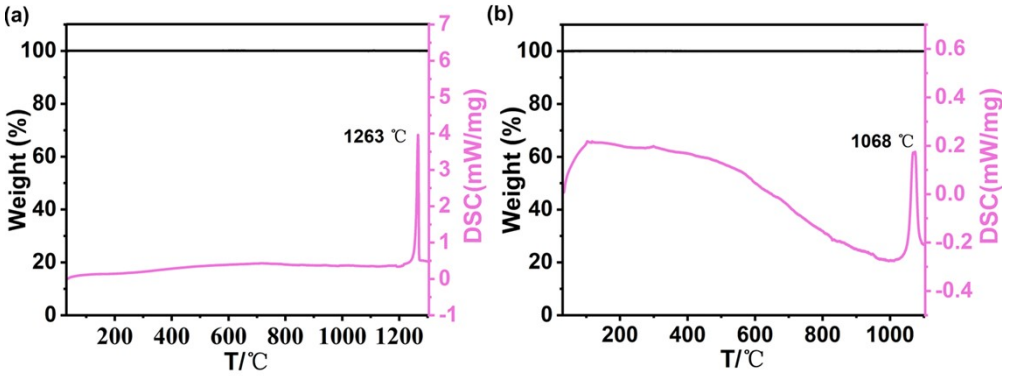


Fig. S5 TG and DSC curves of $LiBePO_4$ and BeP_2O_6.

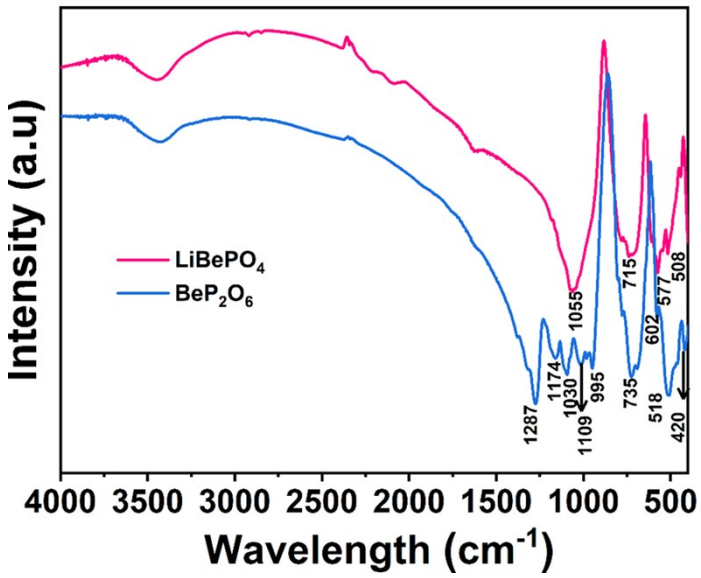


Fig. S6 IR spectra of $LiBePO_4$ and BeP_2O_6.

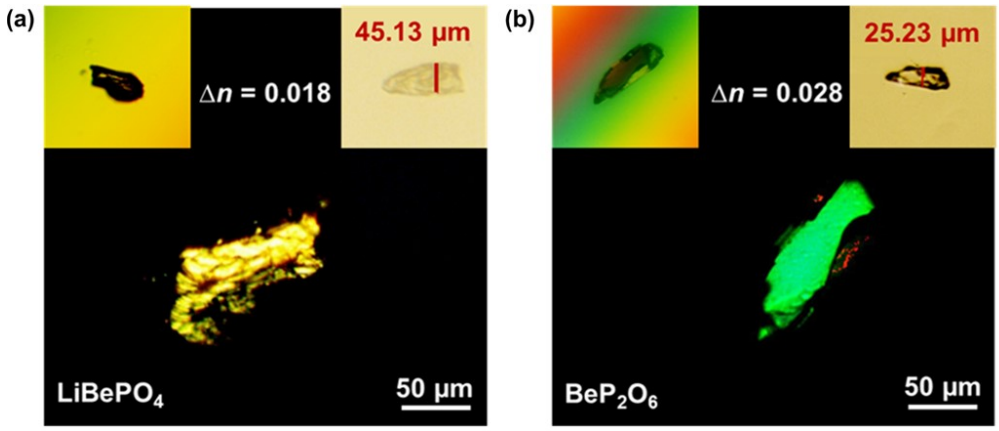


Fig. S7 Birefringence measurements of (a) $LiBePO_4$ and (b) BeP_2O_6.

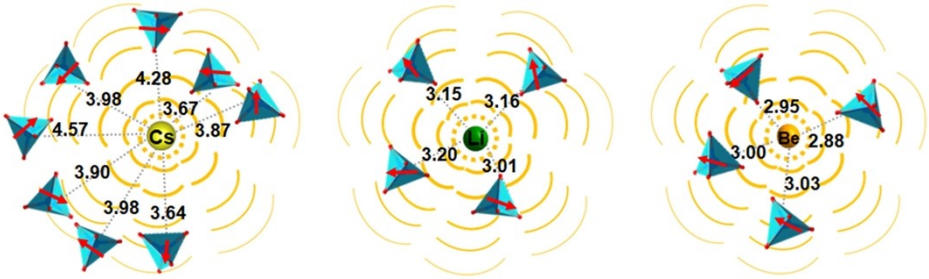


Fig. S8 Arrangement uniformity change of the PO_4 surrounding Cs^+, Li^+ and Be^{2+} in $Cs_4LiBe_4P_7O_{24}$.

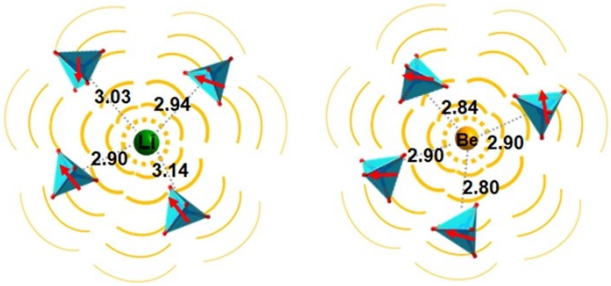


Fig. S9 Arrangement uniformity change of the PO_4 surrounding Li^+ and Be^{2+} in $LiBePO_4$.

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