

Bi₃₂Cd₃P₁₀O₇₆: A New Congruently-Melting Nonlinear Optical Crystal with Large SHG Response and Wide Transparent Region

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Table S1. Crystal data and structure refinement for Bi₃₂Cd₃P₁₀O₇₆.

Empirical formula	Bi ₃₂ Cd ₃ P ₁₀ O ₇₆
Formula weight	8550.26
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2
Unit cell dimensions	$a = 19.3185(5)$ Å $b = 11.3350(3)$ Å $c = 16.3185(6)$ Å $\beta = 101.3600(10)^\circ$
Volume	3503.34(18) Å ³
Z	2
Density (calculated)	8.105 g/cm ³
Absorption coefficient	81.277 mm ⁻¹
F(000)	7116
Theta range for data collection	2.273 to 28.302°.
Index ranges	-25 ≤ h ≤ 25, -15 ≤ k ≤ 15, -21 ≤ l ≤ 21
Reflections collected	31989
Independent reflections	8674 [R _{int} = 0.0773]
Completeness to theta = 25.242°	99.9 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8674 / 86 / 577
Goodness-of-fit on F ²	0.926
Final R indices [I > 2σ(I)]	R ₁ = 0.0453, wR ₂ = 0.0848
R indices (all data)	R ₁ = 0.0649, wR ₂ = 0.0966
Flack parameter	0.04(2)
Extinction coefficient	0.0000278(19)
Largest diff. peak and hole	2.205 and -2.942 e·Å ⁻³

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

for $\text{Bi}_{32}\text{Cd}_3\text{P}_{10}\text{O}_{76}$. $U_{\text{(eq)}}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	x	y	z	$U_{\text{(eq)}}$
Bi(1)	1247(1)	3502(1)	970(1)	23(1)
Bi(2)	409(1)	-1571(1)	-1038(1)	24(1)
Bi(3)	-1618(1)	-1722(1)	-4969(1)	26(1)
Bi(4)	2085(1)	178(1)	-978(1)	25(1)
Bi(5)	2315(1)	1555(1)	3248(1)	23(1)
Bi(6)	606(1)	6247(1)	2982(1)	27(1)
Bi(7)	1209(1)	289(1)	1061(1)	24(1)
Bi(8)	-506(1)	-4895(1)	1001(1)	22(1)
Bi(9)	1061(1)	-1972(2)	-3113(1)	36(1)
Bi(10)	2208(1)	-1705(1)	2938(1)	25(1)
Bi(11)	485(1)	3094(1)	2952(1)	25(1)
Bi(12)	2725(1)	-1407(1)	1025(1)	29(1)
Bi(13)	1620(1)	5052(2)	4791(1)	36(1)
Bi(14)	3881(1)	-153(2)	3130(2)	31(1)
Cd(14)	3881(1)	-153(2)	3130(2)	31(1)
Bi(15)	2013(1)	-3153(2)	-1124(1)	26(1)
Cd(15)	2013(1)	-3153(2)	-1124(1)	26(1)
Bi(16)	1162(1)	1593(2)	-3042(1)	25(1)
Cd(16)	1162(1)	1593(2)	-3042(1)	25(1)
Bi(17)	0	3407(3)	5000	27(1)
Cd(17)	0	3407(3)	5000	27(1)
Bi(18)	0	-3438(3)	-5000	37(1)
Cd(18)	0	-3438(3)	-5000	37(1)
Bi(19)	0	-56(2)	-5000	27(1)
Cd(19)	0	-56(2)	-5000	27(1)
P(1)	1208(5)	-3162(10)	809(6)	25(2)
P(2)	542(5)	1873(10)	-1007(6)	19(2)
P(3)	2234(6)	4695(10)	2945(7)	28(2)
P(4)	-480(5)	-347(10)	-3050(6)	22(2)
P(5)	1565(5)	1795(11)	5070(6)	24(2)
O(1)	1392(11)	-1270(20)	-1357(15)	26(5)
O(2)	2119(12)	-530(20)	1885(14)	29(5)
O(3)	-358(12)	6539(18)	3453(14)	20(5)

O(4)	-691(13)	-1510(20)	-5444(17)	32(6)
O(5)	742(11)	4629(18)	3706(13)	19(5)
O(6)	2074(14)	100(20)	369(14)	33(7)
O(7)	2232(11)	3740(20)	645(15)	27(5)
O(8)	1606(17)	4180(20)	2296(17)	48(8)
O(9)	2776(13)	-171(19)	3540(14)	25(5)
O(10)	-1099(12)	-3300(20)	-4356(13)	23(5)
O(11)	995(15)	2810(20)	-441(16)	40(7)
O(12)	1715(11)	1920(20)	1404(14)	27(5)
O(13)	-1497(13)	-5090(20)	1392(16)	28(6)
O(14)	3143(10)	1780(20)	2441(13)	24(5)
O(15)	1011(19)	2500(30)	4460(20)	67(11)
O(16)	2447(19)	3750(20)	3635(19)	65(11)
O(17)	751(14)	4870(20)	5436(17)	32(6)
O(18)	-47(13)	4650(20)	2243(15)	29(6)
O(19)	504(18)	-3520(40)	990(40)	120(20)
O(20)	1080(20)	-2010(30)	291(18)	61(10)
O(21)	684(16)	670(30)	-581(19)	54(9)
O(22)	-15(17)	-1230(30)	-2456(17)	52(9)
O(23)	1864(12)	2940(20)	-2471(17)	32(6)
O(24)	425(12)	2990(20)	-3506(16)	29(6)
O(25)	3304(14)	1980(20)	4037(17)	45(8)
O(26)	-209(15)	2150(30)	-1180(30)	74(12)
O(27)	2870(20)	4920(30)	2500(20)	66(11)
O(28)	-731(13)	-3200(20)	1437(14)	32(6)
O(29)	1998(14)	5810(20)	3341(17)	37(6)
O(30)	1500(20)	-4070(30)	350(20)	67(10)
O(31)	-620(30)	-880(50)	-3950(30)	51(15)
O(32)	-820(30)	370(50)	-2480(30)	41(12)
O(33)	10(20)	230(40)	-3570(30)	29(10)
O(34)	1775(19)	2490(30)	5890(20)	17(8)
O(35)	1980(40)	1030(60)	4600(40)	73(19)
O(36)	1220(40)	1000(70)	5560(40)	70(20)
O(37)	650(30)	2050(50)	-1920(30)	44(14)
O(38)	1820(30)	-2970(40)	1590(30)	32(11)

Table S3. Selected bond lengths (Å) and angles (deg) for Bi₃₂Cd₃P₁₀O₇₆.

Bi(1)-O(12)	2.07(2)	O(2)-Bi(7)-O(21)	140.5(9)
Bi(1)-O(7)	2.09(2)	O(6)-Bi(7)-O(21)	71.5(10)
Bi(1)-O(8)	2.27(3)	O(32)#1-Bi(7)-O(21)	140.1(14)
Bi(1)-O(11)	2.39(3)	O(18)#8-Bi(8)-O(28)	88.6(9)
Bi(1)-O(26)#1	2.60(3)	O(18)#8-Bi(8)-O(13)	85.4(9)
Bi(2)-O(28)#1	2.09(2)	O(28)-Bi(8)-O(13)	75.0(9)
Bi(2)-O(1)	2.09(2)	O(18)#8-Bi(8)-O(19)	88.8(14)
Bi(2)-O(22)	2.33(3)	O(28)-Bi(8)-O(19)	69.4(12)
Bi(2)-O(20)	2.35(3)	O(13)-Bi(8)-O(19)	144.1(12)
Bi(2)-O(21)	2.67(3)	O(3)#4-Bi(9)-O(14)#5	88.1(9)
Bi(3)-O(4)	2.10(2)	O(3)#4-Bi(9)-O(4)#3	82.3(8)
Bi(3)-O(25)#2	2.17(2)	O(14)#5-Bi(9)-O(4)#3	132.3(9)
Bi(3)-O(10)	2.19(2)	O(3)#4-Bi(9)-O(25)#5	80.1(8)
Bi(3)-O(31A)	2.45(6)	O(14)#5-Bi(9)-O(25)#5	67.0(8)
Bi(3)-O(31)	2.48(5)	O(4)#3-Bi(9)-O(25)#5	65.4(8)
Bi(3)-O(16)#2	2.67(3)	O(3)#4-Bi(9)-O(22)	81.3(9)
Bi(3)-O(36A)#1	2.73(6)	O(14)#5-Bi(9)-O(22)	121.6(8)
Bi(4)-O(7)#5	2.10(2)	O(4)#3-Bi(9)-O(22)	102.9(8)
Bi(4)-O(1)	2.13(2)	O(25)#5-Bi(9)-O(22)	159.2(9)
Bi(4)-O(6)	2.20(2)	O(23)#5-Bi(10)-O(2)	76.8(9)
Bi(4)-O(27)#5	2.53(3)	O(23)#5-Bi(10)-O(9)	85.9(10)
Bi(5)-O(25)	2.14(2)	O(2)-Bi(10)-O(9)	79.7(9)
Bi(5)-O(9)	2.16(2)	O(23)#5-Bi(10)-O(34A)#9	88.1(18)
Bi(5)-O(14)	2.28(2)	O(2)-Bi(10)-O(34A)#9	146.6(18)
Bi(5)-O(35A)	2.44(5)	O(9)-Bi(10)-O(34A)#9	69.5(17)
Bi(5)-O(35)	2.49(7)	O(23)#5-Bi(10)-O(38)	73.5(14)
Bi(5)-O(16)	2.57(3)	O(2)-Bi(10)-O(38)	72.7(13)
Bi(6)-O(5)	2.17(2)	O(9)-Bi(10)-O(38)	148.5(13)
Bi(6)-O(3)	2.17(2)	O(23)#5-Bi(10)-O(34)#9	68.3(11)
Bi(6)-O(10)#7	2.31(2)	O(2)-Bi(10)-O(34)#9	136.8(10)
Bi(6)-O(18)	2.39(2)	O(9)-Bi(10)-O(34)#9	73.3(10)
Bi(6)-O(29)	2.68(3)	O(38)-Bi(10)-O(34)#9	118.3(14)
Bi(7)-O(12)	2.11(2)	O(23)#5-Bi(10)-O(38A)	86(2)
Bi(7)-O(2)	2.20(2)	O(2)-Bi(10)-O(38A)	75(2)
Bi(7)-O(6)	2.20(2)	O(9)-Bi(10)-O(38A)	154(2)
Bi(7)-O(32)#1	2.56(5)	O(34A)#9-Bi(10)-O(38A)	134(3)
Bi(7)-O(21)	2.71(3)	O(5)-Bi(11)-O(24)#1	85.4(9)
Bi(8)-O(18)#8	2.11(2)	O(5)-Bi(11)-O(18)	71.8(8)
Bi(8)-O(28)	2.13(2)	O(24)#1-Bi(11)-O(18)	86.1(9)
Bi(8)-O(13)	2.14(3)	O(5)-Bi(11)-O(15)	69.9(9)
Bi(8)-O(19)	2.50(3)	O(24)#1-Bi(11)-O(15)	77.3(11)
Bi(9)-O(3)#4	2.17(2)	O(18)-Bi(11)-O(15)	139.1(9)
Bi(9)-O(14)#5	2.22(2)	O(5)-Bi(11)-O(37)#1	140.2(11)

Bi(9)-O(4)#3	2.38(3)	O(24)#1-Bi(11)-O(37)#1	67.0(12)
Bi(9)-O(25)#5	2.43(3)	O(18)-Bi(11)-O(37)#1	78.1(12)
Bi(9)-O(22)	2.66(3)	O(15)-Bi(11)-O(37)#1	126.2(14)
Bi(10)-O(23)#5	2.12(2)	O(13)#10-Bi(12)-O(2)	86.6(9)
Bi(10)-O(2)	2.15(2)	O(13)#10-Bi(12)-O(6)	84.2(10)
Bi(10)-O(9)	2.18(2)	O(2)-Bi(12)-O(6)	69.5(8)
Bi(10)-O(34A)#9	2.59(7)	O(13)#10-Bi(12)-O(23)#5	82.2(9)
Bi(10)-O(38)	2.60(5)	O(2)-Bi(12)-O(23)#5	68.9(8)
Bi(10)-O(34)#9	2.62(4)	O(6)-Bi(12)-O(23)#5	136.7(8)
Bi(10)-O(38A)	2.70(10)	O(13)#10-Bi(12)-O(7)#5	94.6(9)
Bi(11)-O(5)	2.13(2)	O(2)-Bi(12)-O(7)#5	136.0(8)
Bi(11)-O(24)#1	2.13(2)	O(6)-Bi(12)-O(7)#5	66.9(7)
Bi(11)-O(18)	2.24(2)	O(23)#5-Bi(12)-O(7)#5	154.9(8)
Bi(11)-O(15)	2.57(3)	O(17)-Bi(13)-O(10)#7	83.6(9)
Bi(11)-O(37)#1	2.75(6)	O(17)-Bi(13)-O(5)	79.9(9)
Bi(12)-O(13)#10	2.12(2)	O(10)#7-Bi(13)-O(5)	72.4(7)
Bi(12)-O(2)	2.23(2)	O(17)-Bi(13)-O(29)	144.5(9)
Bi(12)-O(6)	2.26(2)	O(10)#7-Bi(13)-O(29)	68.5(8)
Bi(12)-O(23)#5	2.45(3)	O(5)-Bi(13)-O(29)	71.1(8)
Bi(12)-O(7)#5	2.75(2)	O(17)-Bi(13)-O(9)#11	74.2(9)
Bi(13)-O(17)	2.16(3)	O(10)#7-Bi(13)-O(9)#11	118.7(7)
Bi(13)-O(10)#7	2.18(2)	O(5)-Bi(13)-O(9)#11	149.9(8)
Bi(13)-O(5)	2.25(2)	O(29)-Bi(13)-O(9)#11	138.3(8)
Bi(13)-O(29)	2.75(3)	O(17)#9-Bi(14)-O(9)	80.1(8)
Bi(13)-O(9)#11	2.76(2)	O(17)#9-Bi(14)-O(3)#13	73.6(8)
Bi(14)-O(17)#9	2.31(3)	O(9)-Bi(14)-O(3)#13	119.5(8)
Bi(14)-O(9)	2.36(3)	O(17)#9-Bi(14)-O(24)#5	73.6(9)
Bi(14)-O(3)#13	2.41(2)	O(9)-Bi(14)-O(24)#5	113.1(8)
Bi(14)-O(24)#5	2.51(3)	O(3)#13-Bi(14)-O(24)#5	110.0(7)
Bi(14)-O(23)#5	2.70(3)	O(17)#9-Bi(14)-O(23)#5	116.4(9)
Bi(14)-O(14)	2.73(3)	O(9)-Bi(14)-O(23)#5	70.4(7)
Bi(15)-O(14)#5	2.11(2)	O(3)#13-Bi(14)-O(23)#5	168.0(8)
Bi(15)-O(13)#1	2.42(2)	O(24)#5-Bi(14)-O(23)#5	69.0(8)
Bi(15)-O(28)#1	2.43(3)	O(17)#9-Bi(14)-O(14)	116.2(8)
Bi(15)-O(1)	2.44(2)	O(9)-Bi(14)-O(14)	72.3(7)
Bi(15)-O(12)#5	2.59(2)	O(3)#13-Bi(14)-O(14)	72.5(7)
Bi(15)-O(7)#5	2.62(2)	O(24)#5-Bi(14)-O(14)	170.0(8)
Bi(16)-O(23)	2.13(3)	O(23)#5-Bi(14)-O(14)	106.5(7)
Bi(16)-O(24)	2.16(2)	O(14)#5-Bi(15)-O(13)#1	34.7(5)
Bi(16)-O(37A)	2.25(7)	O(14)#5-Bi(15)-O(28)#1	141.2(5)
Bi(16)-O(37)	2.30(5)	O(13)#1-Bi(15)-O(28)#1	177.22(9)
Bi(16)-O(33A)	2.37(6)	O(14)#5-Bi(15)-O(1)	121.50(8)
Bi(16)-O(36)#14	2.41(7)	O(13)#1-Bi(15)-O(1)	60.06(6)
Bi(16)-O(34)#14	2.51(4)	O(28)#1-Bi(15)-O(1)	79.1(9)

Bi(16)-O(27)#5	2.69(3)	O(14)#5-Bi(15)-O(12)#5	81.4(7)
Bi(16)-O(33)	2.71(5)	O(13)#1-Bi(15)-O(12)#5	64.9(8)
Bi(17)-O(17)	2.22(3)	O(28)#1-Bi(15)-O(12)#5	84.7(9)
Bi(17)-O(17)#15	2.22(3)	O(1)-Bi(15)-O(12)#5	126.4(7)
Bi(17)-O(24)#1	2.46(3)	O(14)#5-Bi(15)-O(7)#5	62.3(8)
Bi(17)-O(24)#16	2.46(3)	O(13)#1-Bi(15)-O(7)#5	76.8(7)
Bi(17)-O(15)#15	2.51(3)	O(28)#1-Bi(15)-O(7)#5	111.6(8)
Bi(17)-O(15)	2.51(3)	O(1)-Bi(15)-O(7)#5	158.1(7)
Bi(18)-O(17)#4	2.43(3)	O(12)#5-Bi(15)-O(7)#5	113.7(8)
Bi(18)-O(17)#17	2.43(3)	O(23)-Bi(16)-O(24)	52.8(6)
Bi(18)-O(3)#4	2.48(2)	O(23)-Bi(16)-O(37A)	99.3(5)
Bi(18)-O(3)#17	2.48(2)	O(24)-Bi(16)-O(37A)	96.8(5)
Bi(18)-O(10)#3	2.55(2)	O(23)-Bi(16)-O(37)	88.82(5)
Bi(18)-O(10)	2.55(2)	O(24)-Bi(16)-O(37)	64.33(5)
Bi(18)-O(4)#3	2.58(3)	O(23)-Bi(16)-O(33A)	87.1(10)
Bi(18)-O(4)	2.58(3)	O(24)-Bi(16)-O(33A)	74.6(19)
Bi(19)-O(4)#3	2.16(2)	O(37A)-Bi(16)-O(33A)	95.8(19)
Bi(19)-O(4)	2.16(2)	O(23)-Bi(16)-O(36)#14	80.0(13)
Bi(19)-O(33)#3	2.36(4)	O(24)-Bi(16)-O(36)#14	75.8(16)
Bi(19)-O(33)	2.36(4)	O(37)-Bi(16)-O(36)#14	143.9(14)
Bi(19)-O(31)#3	2.46(5)	O(23)-Bi(16)-O(34)#14	71.4(14)
Bi(19)-O(31)	2.46(5)	O(24)-Bi(16)-O(34)#14	79(2)
Bi(19)-O(36A)#14	2.55(6)	O(37)-Bi(16)-O(34)#14	117.9(18)
Bi(19)-O(36A)#1	2.55(6)	O(36)#14-Bi(16)-O(34)#14	91.4(19)
Bi(19)-O(36)#14	2.65(7)	O(23)-Bi(16)-O(27)#5	158(2)
Bi(19)-O(36)#1	2.65(7)	O(24)-Bi(16)-O(27)#5	70.6(11)
P(1)-O(38A)	1.36(10)	O(37)-Bi(16)-O(27)#5	80.2(11)
P(1)-O(30)	1.44(3)	O(36)#14-Bi(16)-O(27)#5	142.8(15)
P(1)-O(19)	1.50(4)	O(34)#14-Bi(16)-O(27)#5	48.2(19)
P(1)-O(20)	1.55(3)	O(23)-Bi(16)-O(33)	91.3(11)
P(1)-O(38)	1.58(5)	O(24)-Bi(16)-O(33)	177.1(10)
P(2)-O(26)	1.46(3)	O(37)-Bi(16)-O(33)	106.3(16)
P(2)-O(21)	1.53(3)	O(36)#14-Bi(16)-O(33)	87.2(19)
P(2)-O(11)	1.56(3)	O(34)#14-Bi(16)-O(33)	96.9(10)
P(2)-O(37)	1.57(5)	O(27)#5-Bi(16)-O(33)	163.9(11)
P(2)-O(37A)	1.61(7)	O(31)-Bi(3)-O(16)#2	143.4(15)
P(3)-O(29)	1.53(3)	O(4)-Bi(3)-O(36A)#1	66.1(15)
P(3)-O(16)	1.55(3)	O(25)#2-Bi(3)-O(36A)#1	120.8(15)
P(3)-O(8)	1.56(3)	O(10)-Bi(3)-O(36A)#1	138.5(15)
P(3)-O(27)	1.57(3)	O(31A)-Bi(3)-O(36A)#1	76(2)
P(4)-O(31A)	1.47(6)	O(31)-Bi(3)-O(36A)#1	64.3(19)
P(4)-O(32)	1.49(4)	O(16)#2-Bi(3)-O(36A)#1	79.1(14)
P(4)-O(32A)	1.51(5)	O(7)#5-Bi(4)-O(1)	78.6(9)
P(4)-O(33)	1.53(4)	O(7)#5-Bi(4)-O(6)	80.8(9)

P(4)-O(22)	1.55(3)	O(1)-Bi(4)-O(6)	97.5(10)
P(4)-O(31)	1.56(5)	O(7)#5-Bi(4)-O(27)#5	91.4(10)
P(4)-O(33A)	1.68(5)	O(1)-Bi(4)-O(27)#5	76.3(11)
P(5)-O(36)	1.44(7)	O(6)-Bi(4)-O(27)#5	170.9(10)
P(5)-O(35)	1.49(7)	O(25)-Bi(5)-O(9)	77.9(10)
P(5)-O(36A)	1.53(6)	O(25)-Bi(5)-O(14)	71.1(10)
P(5)-O(15)	1.53(3)	O(9)-Bi(5)-O(14)	85.5(9)
P(5)-O(34)	1.53(4)	O(25)-Bi(5)-O(35A)	66.7(14)
P(5)-O(35A)	1.58(5)	O(9)-Bi(5)-O(35A)	83.8(13)
P(5)-O(34A)	1.61(7)	O(14)-Bi(5)-O(35A)	137.7(12)
O(31)-O(33)	1.77(7)	O(25)-Bi(5)-O(35)	83.0(18)
O(31A)-O(32A)	1.78(8)	O(9)-Bi(5)-O(35)	76.0(17)
O(12)-Bi(1)-O(7)	80.8(9)	O(14)-Bi(5)-O(35)	150.8(16)
O(12)-Bi(1)-O(8)	86.4(9)	O(25)-Bi(5)-O(16)	66.4(10)
O(7)-Bi(1)-O(8)	94.4(11)	O(9)-Bi(5)-O(16)	143.7(9)
O(12)-Bi(1)-O(11)	92.1(9)	O(14)-Bi(5)-O(16)	89.3(10)
O(7)-Bi(1)-O(11)	79.6(10)	O(35A)-Bi(5)-O(16)	76.2(14)
O(8)-Bi(1)-O(11)	174.0(11)	O(35)-Bi(5)-O(16)	92.5(17)
O(12)-Bi(1)-O(26)#1	75.0(9)	O(5)-Bi(6)-O(3)	87.5(8)
O(7)-Bi(1)-O(26)#1	150.9(10)	O(5)-Bi(6)-O(10)#7	71.3(8)
O(8)-Bi(1)-O(26)#1	100.0(12)	O(3)-Bi(6)-O(10)#7	80.9(8)
O(11)-Bi(1)-O(26)#1	85.3(11)	O(5)-Bi(6)-O(18)	68.3(8)
O(28)#1-Bi(2)-O(1)	74.0(9)	O(3)-Bi(6)-O(18)	83.7(8)
O(28)#1-Bi(2)-O(22)	84.6(9)	O(10)#7-Bi(6)-O(18)	137.2(8)
O(1)-Bi(2)-O(22)	83.4(10)	O(5)-Bi(6)-O(29)	73.6(8)
O(28)#1-Bi(2)-O(20)	87.7(10)	O(3)-Bi(6)-O(29)	147.4(8)
O(1)-Bi(2)-O(20)	84.5(11)	O(10)#7-Bi(6)-O(29)	68.0(8)
O(22)-Bi(2)-O(20)	167.1(12)	O(18)-Bi(6)-O(29)	112.2(8)
O(28)#1-Bi(2)-O(21)	150.5(10)	O(12)-Bi(7)-O(2)	86.3(9)
O(1)-Bi(2)-O(21)	77.0(10)	O(12)-Bi(7)-O(6)	82.0(10)
O(22)-Bi(2)-O(21)	97.4(10)	O(2)-Bi(7)-O(6)	71.2(8)
O(20)-Bi(2)-O(21)	84.2(9)	O(12)-Bi(7)-O(32)#1	86.1(13)
O(4)-Bi(3)-O(25)#2	74.9(11)	O(2)-Bi(7)-O(32)#1	78.7(14)
O(4)-Bi(3)-O(10)	85.0(9)	O(6)-Bi(7)-O(32)#1	148.1(14)
O(25)#2-Bi(3)-O(10)	75.4(9)	O(12)-Bi(7)-O(21)	100.7(9)
O(4)-Bi(3)-O(31A)	92.3(16)		
O(25)#2-Bi(3)-O(31A)	149.3(16)		
O(10)-Bi(3)-O(31A)	75.9(16)		
O(4)-Bi(3)-O(31)	66.2(13)		
O(25)#2-Bi(3)-O(31)	133.7(15)		
O(10)-Bi(3)-O(31)	77.3(15)		
O(4)-Bi(3)-O(16)#2	98.3(11)		
O(25)#2-Bi(3)-O(16)#2	64.2(10)		
O(10)-Bi(3)-O(16)#2	136.6(9)		

Symmetry transformations used to generate equivalent atoms:

#1 $-x, y, -z$ #2 $x-1/2, y-1/2, z-1$ #3 $-x, y, -z-1$
#4 $-x, y-1, -z$ #5 $-x+1/2, y-1/2, -z$ #6 $-x+1/2, y+1/2, -z$
#7 $-x, y+1, -z$ #8 $x, y-1, z$ #9 $-x+1/2, y-1/2, -z+1$
#10 $x+1/2, y+1/2, z$ #11 $-x+1/2, y+1/2, -z+1$ #12 $x, y+1, z+1$
#13 $x+1/2, y-1/2, z$ #14 $x, y, z-1$ #15 $-x, y, -z+1$
#16 $x, y, z+1$ #17 $x, y-1, z-1$ #18 $x-1/2, y+1/2, z$
#19 $x-1/2, y-1/2, z$ #20 $x+1/2, y+1/2, z+1$ #21 $x, y+1, z$

Table S4 Dipole moments (in Debye) of PO₄, BiO_n (n = 4, 5, 6) and Bi_xCd_{1-x}O_n (n = 6, 7, 8) polyhedra in the unit cell.

Species	Dipole moment		
	X-axis	Y-axis	Z-axis
Bi(1)O ₅	0	-14.755	0
Bi(2)O ₅	0	-22.160	0
Bi(3)O ₆	0	-27.640	0
Bi(4)O ₄	0	-37.151	0
Bi(5)O ₅	0	-12.700	0
Bi(6)O ₅	0	-22.162	0
Bi(7)O ₅	0	7.124	0
Bi(8)O ₄	0	18.115	0
Bi(9)O ₅	0	-26.513	0
Bi(10)O ₅	0	25.940	0
Bi(11)O ₆	0	34.209	0
Bi(12)O ₅	0	30.717	0
Bi(13)O ₆	0	-0.680	0
Bi(14)O ₇	0	-6.279	0
Bi(15)O ₆	0	23.964	0
Bi(16)O ₇	0	40.297	0
Bi(17)O ₆	0	25.140	0
Bi(18)O ₈	0	19.332	0
Bi(19)O ₈	0	-34.273	0
$\Sigma \text{Bi}(x)\text{O}_y$	0	20.525	0
Cd (14)O ₇	0	2.799	0
Cd (15)O ₆	0	-3.862	0
Cd (16)O ₇	0	23.658	0
Cd (17)O ₆	0	3.854	0
Cd (18)O ₈	0	22.727	0
Cd (19)O ₈	0	-9.236	0
$\Sigma \text{Cd}(x)\text{O}_y$	0	39.941	0
P(1)O ₄	0	-5.328	0
P(2)O ₄	0	6.120	0
P(3)O ₄	0	-2.366	0
P(4)O ₄	0	0.908	0
P(5)O ₄	0	-12.709	0
$\Sigma \text{P}(x)\text{O}_y$	0	-13.375	0

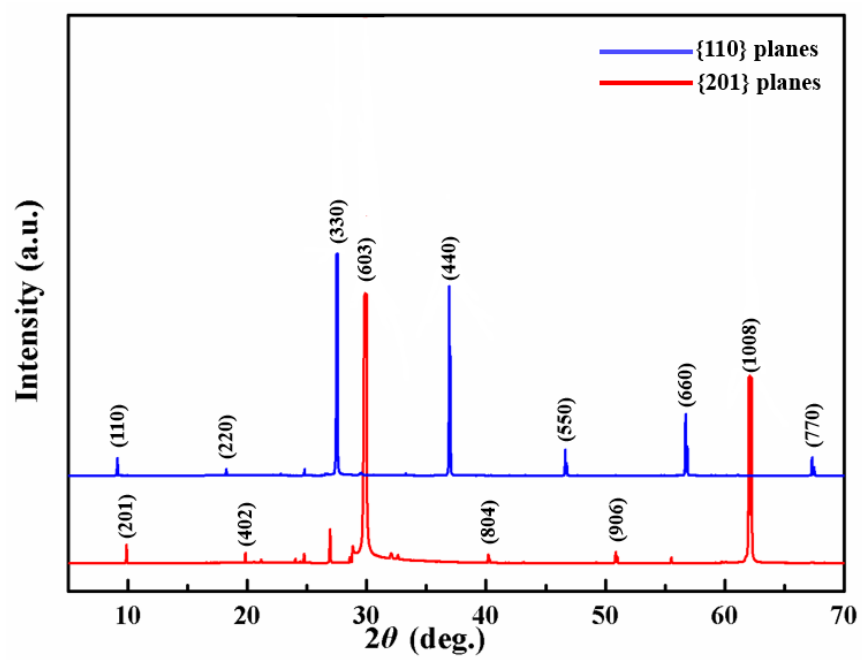
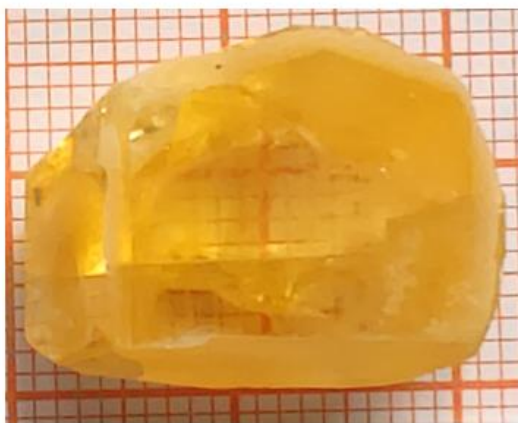
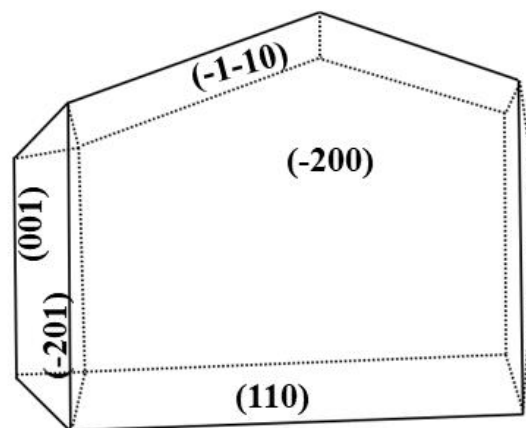


Figure S1. XRD patterns of (201) and (110) planes of BCPO.



(a)



(b)

Figure S2. Photograph (a) and morphology (b) of the BCPO crystal grown with $[001]$ -orientated seed.

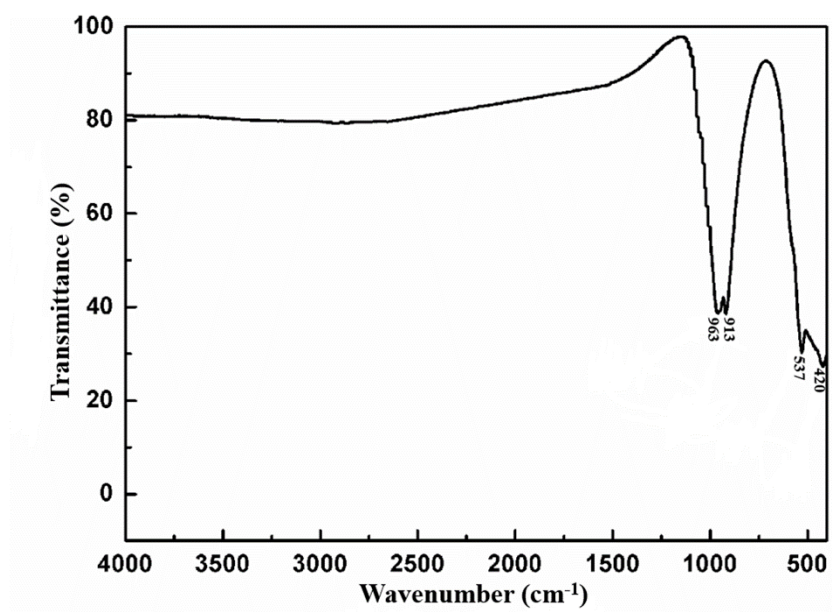


Figure S3. IR spectrum of BCPO.

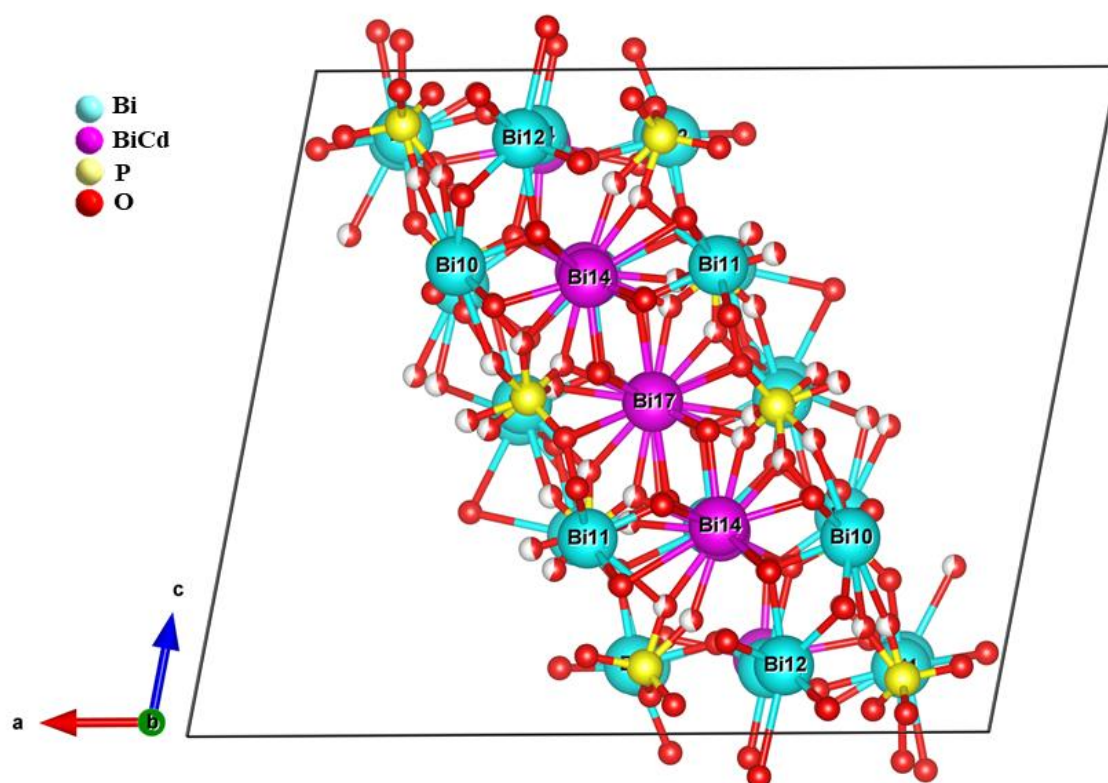


Figure S4. The Bi-O and Bi/Cd-O polyhedra in the unit cell.