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Nonlinear Optical Response Mechanism of Noncentrosymmetric Lead Borate $Pb_6[B_4O_7(OH)_2]_3$ with Three Crystallographically Independent $[B_4O_7(OH)_2]^{4-}$ Chains

(Electronic Supplementary Information: 12 pages)

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Single crystal X-ray crystallography. A crystal of $Pb_6[B_4O_7(OH)_2]_3$ with dimensions of 0.21mm × 0.17 mm× 0.10 mm was chosen for single crystal data collection. The structural data were collected by a Bruker SMART APEX II CCD single-crystal diffractometer equipped monochromatic Mo Kα radiation (λ = 0.71073 Å) at 293 K, and obtained data was integrated with a SAINT program.[1] Numerical absorption corrections were finished by the SCALE program for the area detector.[1] Programs from the SHELXTL crystallographic software package were used for all calculations.[2] All the non-hydrogen atoms were solved by direct methods and refined by full-matrix least-squares techniques with anisotropic thermal parameters. Hydrogen atoms were placed by geometrical method. Final least-squares refinement is on F_o^2 with data having $F_o^2 \geq 2\sigma(F_o^2)$. The final structure was checked for missing symmetry elements with PLATON.[3]

Table S1. Crystal data and structure refinements for $Pb_6[B_4O_7(OH)_2]_3$[a]

Empirical formula	$Pb_6[B_4O_7(OH)_2]_3$
Formula weight ($g \cdot mol^{-1}$)	1810.91
Crystal system	Trigonal
Space group	$P3_2$(No.145)
a / Å	11.7732(5)
b / Å	11.7732(5)
c / Å	13.345(11)
V / $Å^3$	1601.8(16)
Z	3
F(000)	2322
Crystal size / mm^3	0.21 × 0.17 × 0.10

ϑ_{max} / °	27.43
Reflections collected / Unique	9741 / 3873
Completeness / %	99.5
GOF on F^2	1.150
R_1, wR_2 (I>2σ(I))[a]	0.0495, 0.1098
R_1, wR_2 (all data)	0.0544, 0.1119
Flack parameter	0.01(3)

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

Table S2. The final coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) of non-hydrogen atoms for $Pb_6[B_4O_7(OH)_2]_3$. ***U*eq** is defined as one-third of the trace of the orthogonalized Uij tensor, and the Bond Valence Sum (BVS) for each atom in asymmetric unit.

Atoms	*x/a*	*y/b*	*z/c*	U_{eq}	BVS
Pb(1)	2591(1)	3986(1)	2027(1)	11(1)	2.1
Pb(2)	5867(1)	7218(1)	3294(1)	12(1)	2.1
Pb(3)	–743(1)	1771(1)	235(1)	12(1)	2.2
Pb(4)	6014(1)	5424(1)	565(1)	10(1)	2.1
Pb(5)	2739(1)	2182(1)	–1039(1)	15(1)	2.0
Pb(6)	9165(1)	5237(1)	–775(1)	11(1)	2.1
B(1)	660(40)	–30(40)	190(30)	15(4)	3.0
B(2)	6020(30)	3400(30)	–890(20)	3(6)	3.1
B(3)	2240(30)	4450(30)	–370(30)	7(6)	3.0

B(4)	420(30)	690(30)	1930(20)	5(6)	3.0
B(5)	2790(30)	6050(30)	3500(30)	10(7)	3.1
B(6)	3760(30)	7390(30)	1920(30)	11(7)	3.0
B(7)	−1200(30)	1530(30)	−2040(30)	12(7)	3.0
B(8)	5580(40)	4390(40)	2910(30)	15(4)	3.0
B(9)	6940(30)	4060(30)	−2600(20)	5(6)	3.0
B(10)	6130(30)	8260(40)	1140(30)	15(4)	3.0
B(11)	−1160(40)	−2180(30)	−260(30)	14(7)	3.1
B(12)	5440(30)	4900(30)	−1900(20)	4(6)	2.8
O(1)	5243(17)	4048(17)	−1029(14)	4(4)	2.1
O(2)	7099(17)	3840(17)	−1548(14)	4(4)	2.1
O(3)	36(18)	430(18)	859(15)	7(4)	2.0
O(4)	10389(19)	5903(19)	1045(15)	10(4)	1.1
O(5)	1630(20)	3140(20)	−245(17)	15(5)	2.0
O(6)	−1317(18)	568(18)	−1313(15)	7(4)	2.1
O(7)	4920(20)	5050(20)	2728(16)	12(4)	1.9
O(8)	6910(20)	9581(19)	693(16)	12(4)	1.2
O(9)	6752(17)	4819(17)	2388(14)	4(4)	1.9
O(10)	2(19)	−1513(19)	234(15)	8(4)	1.9
O(11)	−40(20)	1520(20)	2341(17)	15(5)	2.0
O(12)	1736(19)	5006(19)	−1017(15)	9(4)	1.8
O(13)	8277(19)	4871(18)	−3077(15)	8(4)	1.9

O(14)	5390(18)	7349(17)	325(14)	4(4)	2.0
O(15)	3273(18)	6194(18)	2479(14)	5(4)	2.2
O(16)	589(19)	360(19)	−842(15)	10(4)	2.0
O(17)	6184(19)	4711(19)	−2741(15)	8(4)	2.1
O(18)	−2570(20)	1160(20)	−2323(17)	19(5)	1.1
O(19)	7058(18)	7871(18)	1548(14)	7(4)	1.2
O(20)	6500(17)	3711(17)	173(14)	4(4)	2.0
O(21)	3370(20)	5240(20)	201(15)	11(4)	1.9
O(22)	3815(18)	6667(18)	4187(14)	7(4)	2.0
O(23)	8130(19)	6500(19)	−188(15)	10(4)	1.8
O(24)	−520(20)	1550(20)	−2911(17)	14(5)	2.1
O(25)	278(19)	3969(19)	1712(15)	9(4)	1.1
O(26)	5250(20)	8190(20)	1961(17)	16(5)	2.0
O(27)	−690(20)	2850(20)	−1565(16)	15(5)	1.1

Table S3. Selected bond distances (Å) and bond angles (deg.) for $Pb_6[B_4O_7(OH)_2]_3$.

Pb(1)-O(15)	2.383(18)	O(6)-Pb(3)-O(5)	93.1(7)
Pb(1)-O(14)[a]	2.526(19)	O(3)-Pb(3)-O(27)	135.2(7)
Pb(1)-O(7)	2.56(2)	O(6)-Pb(3)-O(27)	56.4(6)
Pb(1)-O(25)	2.745(19)	O(5)-Pb(3)-O(27)	73.5(7)
Pb(1)-O(21)	2.76(2)	O(3)-Pb(3)-O(8)[b]	80.5(6)
Pb(2)-O(7)	2.34(2)	O(6)-Pb(3)-O(8)[b]	77.4(6)

Pb(2)-O(26)	2.41(2)	O(5)-Pb(3)-O(8)[b]	159.0(6)
Pb(2)-O(22)	2.472(18)	O(27)-Pb(3)-O(8)[b]	114.5(6)
Pb(2)-O(19)	2.628(19)	O(23)-Pb(4)-O(20)	74.4(6)
Pb(3)-O(3)	2.339(18)	O(23)-Pb(4)-O(1)	86.1(6)
Pb(3)-O(6)	2.40(2)	O(20)-Pb(4)-O(1)	56.4(6)
Pb(3)-O(5)	2.52(2)	O(23)-Pb(4)-O(14)	98.8(6)
Pb(3)-O(27)	2.71(2)	O(20)-Pb(4)-O(14)	160.7(6)
Pb(3)-O(8)[b]	2.74(2)	O(1)-Pb(4)-O(14)	105.8(6)
Pb(4)-O(23)	2.38(2)	O(5)-Pb(5)-O(16)	77.8(7)
Pb(4)-O(20)	2.413(18)	O(5)-Pb(5)-O(24)[c]	89.6(7)
Pb(4)-O(1)	2.550(18)	O(16)-Pb(5)-O(24)[c]	56.7(7)
Pb(4)-O(14)	2.728(18)	O(5)-Pb(5)-O(1)	104.5(7)
Pb(5)-O(5)	2.36(2)	O(16)-Pb(5)-O(1)	171.0(6)
Pb(5)-O(16)	2.377(19)	O(24)[c]-Pb(5)-O(1)	114.5(6)
Pb(5)-O(24)[c]	2.59(2)	O(17)[d]-Pb(6)-O(2)	89.5(7)
Pb(5)-O(1)	2.654(18)	O(17)[d]-Pb(6)-O(23)	96.0(7)
Pb(6)-O(17)[d]	2.33(2)	O(2)-Pb(6)-O(23)	85.0(6)
Pb(6)-O(2)	2.384(18)	O(17)[d]-Pb(6)-O(4)	56.2(6)
Pb(6)-O(23)	2.474(19)	O(2)-Pb(6)-O(4)	142.4(6)
Pb(6)-O(4)	2.73(2)	O(23)-Pb(6)-O(4)	83.9(6)
B(1)-O(3)	1.43(4)	O(3)-B(1)-O(16)	110(3)
B(1)-O(16)	1.47(4)	O(3)-B(1)-O(24)[c]	112(3)

B(1)-O(24)[c]	1.48(4)	O(16)-B(1)-O(24)[c]	107(3)
B(1)-O(10)	1.51(4)	O(3)-B(1)-O(10)	110(3)
B(2)-O(2)	1.41(3)	O(16)-B(1)-O(10)	109(3)
B(2)-O(1)	1.47(3)	O(24)[c]-B(1)-O(10)	108(2)
B(2)-O(20)	1.50(3)	O(2)-B(2)-O(1)	114(2)
B(2)-O(9)[e]	1.50(3)	O(2)-B(2)-O(20)	110(2)
B(3)-O(5)	1.34(4)	O(1)-B(2)-O(20)	104(2)
B(3)-O(12)	1.39(4)	O(2)-B(2)-O(9)[e]	110(2)
B(3)-O(21)	1.40(4)	O(1)-B(2)-O(9)[e]	112(2)
B(4)-O(11)	1.44(4)	O(20)-B(2)-O(9)[e]	106(2)
B(4)-O(3)	1.48(4)	O(5)-B(3)-O(12)	120(3)
B(4)-O(16)[c]	1.51(4)	O(5)-B(3)-O(21)	119(3)
B(4)-O(6)[c]	1.51(3)	O(12)-B(3)-O(21)	121(3)
B(5)-O(22)	1.40(4)	O(11)-B(4)-O(3)	109(2)
B(5)-O(15)	1.46(4)	O(11)-B(4)-O(16)[c]	108(2)
B(5)-O(14)[a]	1.49(4)	O(3)-B(4)-O(16)[c]	109(2)
B(5)-O(21)[a]	1.54(4)	O(11)-B(4)-O(6)[c]	111(2)
B(6)-O(15)	1.44(4)	O(3)-B(4)-O(6)[c]	110(2)
B(6)-O(22)[f]	1.49(4)	O(16)[c]-B(4)-O(6)[c]	109(2)
B(6)-O(12)[a]	1.50(4)	O(22)-B(5)-O(15)	111(2)
B(6)-O(26)	1.52(4)	O(22)-B(5)-O(14)[a]	114(2)
B(7)-O(24)	1.41(4)	O(15)-B(5)-O(14)[a]	105(2)

B(7)-O(6)	1.45(4)	O(22)-B(5)-O(21)[a]	112(2)
B(7)-O(18)	1.49(4)	O(15)-B(5)-O(21)[a]	107(2)
B(7)-O(27)	1.49(4)	O(14)[a]-B(5)-O(21)[a]	107(2)
B(8)-O(13)[g]	1.35(4)	O(15)-B(6)-O(22)[f]	112(2)
B(8)-O(7)	1.37(4)	O(15)-B(6)-O(12)[a]	113(3)
B(8)-O(9)	1.39(4)	O(22)[f]-B(6)-O(12)[a]	105(2)
B(9)-O(17)	1.45(3)	O(15)-B(6)-O(26)	111(2)
B(9)-O(2)	1.45(4)	O(22)[f]-B(6)-O(26)	109(2)
B(9)-O(20)[e]	1.49(3)	O(12)[a]-B(6)-O(26)	107(2)
B(9)-O(13)	1.51(3)	O(24)-B(7)-O(6)	113(3)
B(10)-O(14)	1.47(4)	O(24)-B(7)-O(18)	109(3)
B(10)-O(26)	1.48(4)	O(6)-B(7)-O(18)	106(3)
B(10)-O(8)	1.48(4)	O(24)-B(7)-O(27)	114(3)
B(10)-O(19)	1.49(4)	O(6)-B(7)-O(27)	111(3)
B(11)-O(23)[b]	1.35(4)	O(18)-B(7)-O(27)	103(2)
B(11)-O(10)	1.36(4)	O(13)[g]-B(8)-O(7)	121(3)
B(11)-O(11)[h]	1.40(4)	O(13)[g]-B(8)-O(9)	123(3)
B(12)-O(1)	1.48(3)	O(7)-B(8)-O(9)	116(3)
B(12)-O(25)[f]	1.49(3)	O(17)-B(9)-O(2)	113(2)
B(12)-O(4)[e]	1.49(3)	O(17)-B(9)-O(20)[e]	109(2)
B(12)-O(17)	1.50(4)	O(2)-B(9)-O(20)[e]	111(2)
O(15)-Pb(1)-O(14)[a]	56.8(6)	O(17)-B(9)-O(13)	109(2)

O(15)-Pb(1)-O(7)	71.2(6)	O(2)-B(9)-O(13)	110(2)
O(14)[a]-Pb(1)-O(7)	86.6(6)	O(20)[e]-B(9)-O(13)	106(2)
O(15)-Pb(1)-O(25)	80.7(6)	O(14)-B(10)-O(26)	112(3)
O(14)[a]-Pb(1)-O(25)	72.5(6)	O(14)-B(10)-O(8)	108(3)
O(7)-Pb(1)-O(25)	151.2(6)	O(26)-B(10)-O(8)	115(3)
O(15)-Pb(1)-O(21)	78.5(6)	O(14)-B(10)-O(19)	107(3)
O(14)[a]-Pb(1)-O(21)	132.4(6)	O(26)-B(10)-O(19)	108(3)
O(7)-Pb(1)-O(21)	94.2(6)	O(8)-B(10)-O(19)	107(2)
O(25)-Pb(1)-O(21)	86.1(6)	O(23)[b]-B(11)-O(10)	120(3)
O(7)-Pb(2)-O(26)	100.7(7)	O(23)[b]-B(11)-O(11)[h]	118(3)
O(7)-Pb(2)-O(22)	89.9(7)	O(10)-B(11)-O(11)[h]	121(3)
O(26)-Pb(2)-O(22)	89.7(7)	O(1)-B(12)-O(25)[f]	112(2)
O(7)-Pb(2)-O(19)	85.8(7)	O(1)-B(12)-O(4)[e]	106(2)
O(26)-Pb(2)-O(19)	56.7(7)	O(25)[f]-B(12)-O(4)[e]	106(2)
O(22)-Pb(2)-O(19)	144.3(6)	O(1)-B(12)-O(17)	113(2)
O(3)-Pb(3)-O(6)	89.9(7)	O(25)[f]-B(12)-O(17)	112(2)
O(3)-Pb(3)-O(5)	80.8(7)	O(4)[e]-B(12)-O(17)	107(2)

Symmetry transformations used to generate equivalent atoms:

(a)–x+y,–x+1,z+1/3 (b) x–1,y–1,z (c)–x+y,–x,z+1/3

(d)–x+y+1,–x+1,z+1/3 (e)–y+1,x–y,z–1/3 (f)–y+1,x–y+1,z–1/3

(g)–y+1,x–y,z+2/3 (h)–y,x–y,z–1/3 (i) x+1,y+1,z

(j)–x+y+1,–x+1,z–2/3

Microphotography.

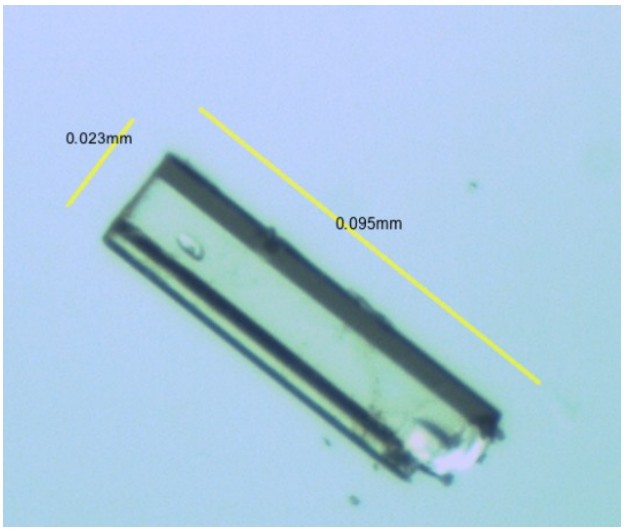

Fig. S1 Microphotography of $Pb_6[B_4O_7(OH)_2]_3$.

Powder XRD. Powder X-ray diffraction (PXRD) was carried out by a Bruker D2 PHASER X-ray diffractometer equipped a diffracted beam monochromator for obtaining Cu Kα radiation whose wavelength is 1.5418 Å. The scan step is 0.02 ° per second with the angular range of 10-70 ° (see Fig. S2).

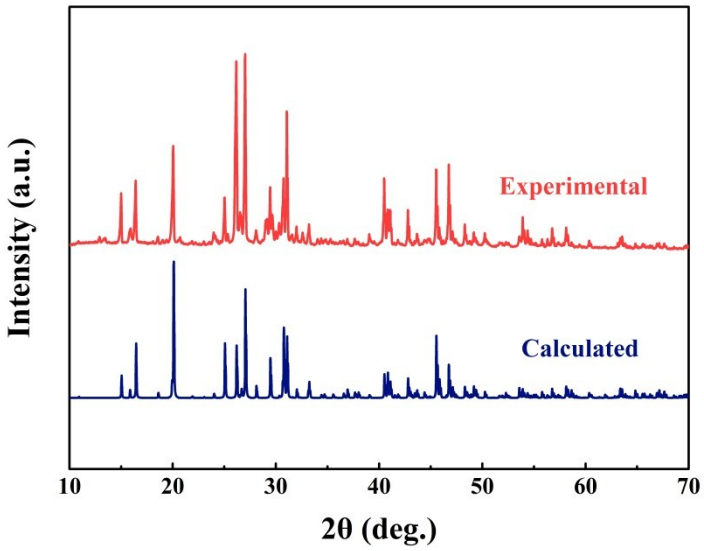

Fig. S2 Experimental and calculated XRD patterns of $Pb_6[B_4O_7(OH)_2]_3$.

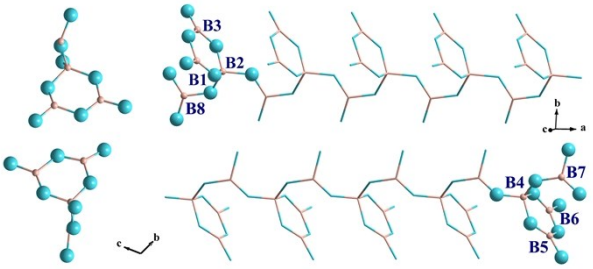

Fig. S3 Two crystallographicly independent $[B_4O_8]^{4-}$ chains in $Bi[B_4O_6(OH)_2]OH$.

IR spectroscopy. The IR spectrum was determined by a Shimadzu IR Affinity-1 Fourier transform infrared spectrometer for the range of 400 to 4000 cm^{-1}. Incidentally, the sample for the IR spectrum measurement is composed by dried high-purity KBr (400 mg) and the polycrystalline powder of $Pb_6[B_4O_7(OH)_2]_3$ (4 mg).

The structural units of $Pb_6[B_4O_7(OH)_2]_3$ were confirmed by IR spectrum (see Fig. S4). The absorption peaks at 1305 cm^{-1} and 955 cm^{-1} were recognized, which could be assigned to the asymmetric stretching vibrations and symmetric stretching vibrations of $[BO_3]^{3-}$. Analogously, the asymmetric and symmetric stretching vibrations of $[BO_4]^{5-}$ groups correspond to the peaks at 1036 and 734 cm^{-1}, respectively. The bending vibrations of $[BO_3]^{3-}$ and $[BO_4]^{5-}$ can also be found in the range of 400-800 cm^{-1}. These peaks in the curve are similar to other reported borates, which confirm the existence of $[BO_3]^{3-}$ and $[BO_4]^{5-}$ groups.[4] Furthermore, the presence of OH^- was shown by the broad absorption peak in the range of near 3450 cm^{-1}.

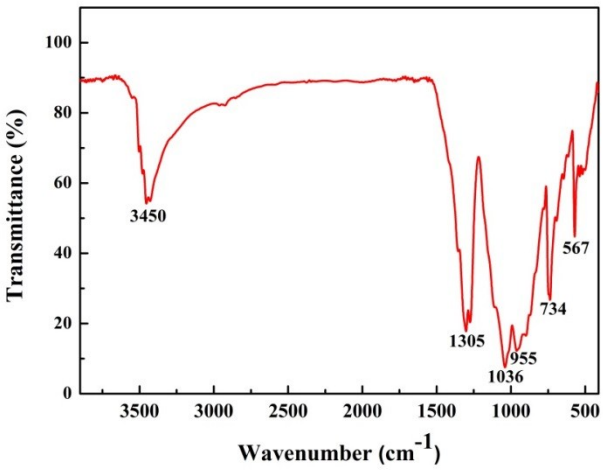

Fig. S4 The IR spectrum of $Pb_6[B_4O_7(OH)_2]_3$.

Notes and references

S1 SAINT, *Version 7.60A; Bruker Analytical X-ray Instruments, Inc.: Madison, WI, 2008.*

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