Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

$BaSc_2(HPO_3)_4(H_2O)_2$: A New Nonlinear Optical Phosphite Exhibiting 3D $[Sc_2(HPO_3)_4]^{2-}$ Anionic Framework and Phase Matchable SHG Effect

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Table S1. Selected Bond lengths for $BaSc_2(HPO_3)_4(H_2O)_2$.

$BaSc_2(HPO_3)_4(H_2O)_2$			
Atom–Atom	Length/Å	Atom–Atom	Length/Å
Ba1–O5	2.850(4)	Sc1–O10[7]	2.101(4)
Ba1–O9[1]	2.994(4)	P3–O9	1.534(4)
Ba1–O9[2]	3.039(4)	P3–O7	1.503(4)
Ba1–O7[2]	2.985(4)	P3–O8	1.498(4)
Ba1–O8[1]	2.850(5)	P1–O12	1.516(5)
Ba1–O6	3.111(5)	P1–O11	1.509(5)
Ba1–O14	2.807(5)	P1–O10	1.516(4)
Ba1[9]–O10	3.173(5)	P2–O1	1.530(5)
Ba1–O14[3]	3.103(6)	P2–O2	1.520(5)
Ba1–O13	2.716(6)	P2–O3	1.500(5)
Sc2–O12[4]	2.077(4)	P4–O5	1.511(4)
Sc2–O4	2.049(4)	P4–O4	1.507(4)
Sc2–O7	2.086(4)	P4–O6	1.519(5)
Sc2–O8[5]	2.090(4)		
Sc2–O6[6]	2.080(4)		
Sc2–O3	2.054(4)		
Sc1–O5	2.084(4)		
Sc1–O9[2]	2.143(4)		
Sc1–O1[7]	2.087(4)		
Sc1–O11	2.040(4)		
Sc1–O2	2.051(4)		

[1]–1/2+x,1–y,–3/2+z; [2]+x,+y,–1+z; [3]–1/2+x,2–y,1/2+z; [4]+x,+y,1+z; [5]–1/2+x,1–y,–1/2+z; [6]1/2+x,1–y,1/2+z; [7]–1/2+x,2–y,–1/2+z; [8]1/2+x,1–y,3/2+z; [9]1/2+x,2–y,–1/2+z; [10]1/2+x,2–y,1/2+z

Table S2. Selected bond angles for $BaSc_2(HPO_3)_4(H_2O)_2$.

$BaSc_2(HPO_3)_4(H_2O)_2$			
Atom–Atom–Atom	Angle/°	Atom–Atom–Atom	Angle/°
P4–O5–Sc1	144.8(3)	O5–Sc1–O9^{2}	84.94(17)
P3–O9–Sc1^{4}	129.5(2)	O5–Sc1–O1^{7}	90.99(17)
P1–O12–Sc2^{9}	139.2(3)	O5–Sc1–O10^{7}	82.70(17)
P2–O1–Sc1^{10}	134.7(3)	O1^{7}–Sc1–O9^{2}	174.20(17)
P4–O4–Sc2	155.6(3)	O1^{7}–Sc1–O10^{7}	91.71(17)
P3–O7–Sc2	150.8(3)	O11–Sc1–O5	175.11(17)
P1–O11–Sc1	150.8(3)	O11–Sc1–O9^{2}	93.17(18)
P2–O2–Sc1	149.7(3)	O11–Sc1–O1^{7}	90.56(19)
P1–O10–Sc1^{10}	153.6(3)	O11–Sc1–O2	91.86(18)
P3–O8–Sc2^{6}	147.4(3)	O11–Sc1–O10^{7}	92.62(17)
P4–O6–Sc2^{5}	138.1(3)	O2–Sc1–O5	92.46(17)
P2–O3–Sc2	143.0(3)	O2–Sc1–O9^{2}	84.80(19)
P4–O5–Ba1	106.1(2)	O2–Sc1–O1^{7}	99.52(19)
P3–O9–Ba1^{8}	98.62(18)	O2–Sc1–O10^{7}	167.86(19)
P3–O9–Ba1^{4}	97.45(19)	O10^{7}–Sc1–O9^{2}	83.69(16)
P3–O7–Ba1^{4}	100.45(19)	O12^{4}–Sc2–O7	88.90(17)
P1–O10–Ba1^{10}	111.6(2)	O12^{4}–Sc2–O8^{6}	86.0(2)
P3–O8–Ba1^{8}	103.5(2)	O12^{4}–Sc2–O6^{3}	178.3(2)
P4–O6–Ba1	94.9(2)	O4–Sc2–O12^{4}	92.36(18)
O7–P3–O9	110.2(2)	O4–Sc2–O7	169.11(18)
O8–P3–O9	107.8(3)	O4–Sc2–O8^{6}	88.73(18)
O8–P3–O7	113.6(3)	O4–Sc2–O6^{3}	86.45(18)
O11–P1–O12	109.0(3)	O4–Sc2–O3	97.42(18)
O11–P1–O10	113.4(3)	O7–Sc2–O8^{6}	80.57(17)
O10–P1–O12	111.5(3)	O6^{3}–Sc2–O7	92.03(17)
O2–P2–O1	111.0(3)	O6^{3}–Sc2–O8^{6}	92.7(2)
O3–P2–O1	111.0(3)	O3–Sc2–O12^{4}	92.1(2)
O3–P2–O2	111.8(3)	O3–Sc2–O7	93.34(18)
O5–P4–O6	107.1(2)	O3–Sc2–O8^{6}	173.64(19)
O4–P4–O5	112.6(2)	O3–Sc2–O6^{3}	89.3(2)

O4–P4–O6	112.1(3)		

[1]–1/2+x,1–y,–3/2+z; [2]+x,+y,–1+z; [3]–1/2+x,2–y,1/2+z; [4]+x,+y,1+z; [5]–1/2+x,1–y,–1/2+z; [6]1/2+x,1–y,1/2+z; [7]–1/2+x,2–y,–1/2+z; [8]1/2+x,1–y,3/2+z; [9]1/2+x,2–y,–1/2+z; [10]1/2+x,2–y,1/2+z

Table S3. Fractional atomic coordinates (Å×10^4) and equivalent isotropic displacement Parameters (Å^2×10^3) for $BaSc_2(HPO_3)_4(H_2O)_2$.

$BaSc_2(HPO_3)_4(H_2O)_2$				
Atom	x	y	z	U(eq)
Ba1	3731.2(5)	5160.3(4)	–335.4(5)	22.41(12)
Sc2	5566.0(12)	6255.8(11)	6855.0(12)	8.6(2)
Sc1	5673.9(12)	8762.1(11)	2057.4(12)	8.9(2)
P3	7721.5(18)	6477.2(18)	10981.3(18)	12.2(3)
P1	8981.1(18)	10898.1(17)	2903.8(18)	12.9(3)
P2	7550.6(18)	8991.4(18)	6148.3(18)	13.8(3)
P4	3113.8(18)	6630.1(17)	2766.4(17)	12.1(3)
O5	3868(5)	7338(4)	1872(5)	15.4(9)
O9	6825(5)	6772(5)	11906(5)	13.7(9)
O12	8978(6)	12191(6)	1895(5)	31.5(12)
O1	9339(5)	9385(5)	7014(5)	18.4(10)
O4	4341(5)	6151(5)	4420(5)	21.6(10)
O7	6559(5)	6005(5)	9309(5)	16.4(9)
O11	7385(6)	10108(5)	2044(5)	19.9(10)
O2	7012(5)	8453(5)	4468(5)	26.0(11)
O10	9409(5)	11399(5)	4565(5)	23.1(11)
O8	9005(5)	5351(5)	11893(5)	27.8(12)
O6	2099(6)	5337(5)	1766(5)	28.2(11)
O14	573(6)	6248(6)	–1972(7)	32.9(13)
O3	7176(6)	7879(5)	7078(5)	32.0(12)
O13	5526(8)	2708(7)	–9(8)	41.5(15)

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

Table S4. Hydrogen Atom Coordinates ($Å \times 10^4$) and Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $BaSc_2(HPO_3)_4(H_2O)_2$.

$BaSc_2(HPO_3)_4(H_2O)_2$				
Atom	x	y	z	U(eq)
H1	10080(70)	9980(60)	2840(70)	4(15)
H2	6770(80)	10170(60)	5910(80)	7
H4	2280(70)	7720(60)	3000(70)	10(15)
H3	8290(70)	7650(70)	10890(70)	18(17)
H14A	–50(100)	6080(90)	–1640(100)	30(30)
H14B	490(100)	7140(40)	–1890(100)	32
H13A	6470(40)	2710(140)	350(130)	100(50)
H13B	5560(130)	2160(120)	690(130)	70(40)

Table S5. The quantitative analysis table of EDS.

Element	AN	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]
O	8	30.69	41.28	67.05
P	15	17.35	23.33	19.58
Ba	56	13.56	18.23	3.45
Sc	21	12.75	17.15	9.92

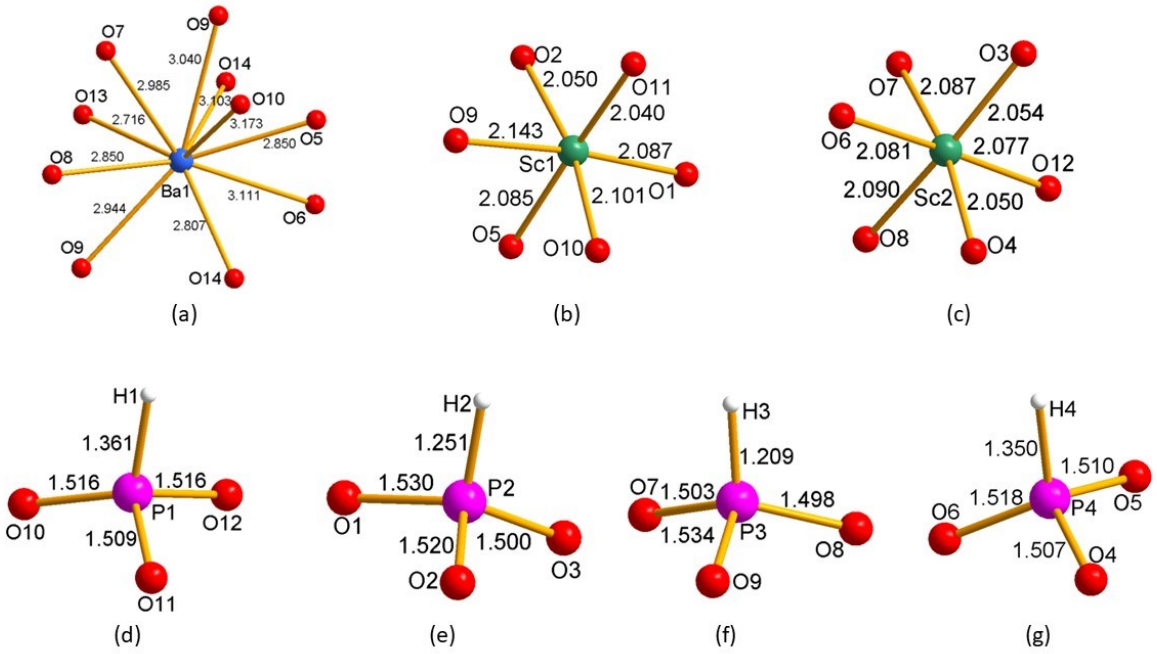

Figure S1. The coordination geometries of Ba, Sc and P atoms in the structure of $BaSc_2(HPO_3)_4(H_2O)_2$.

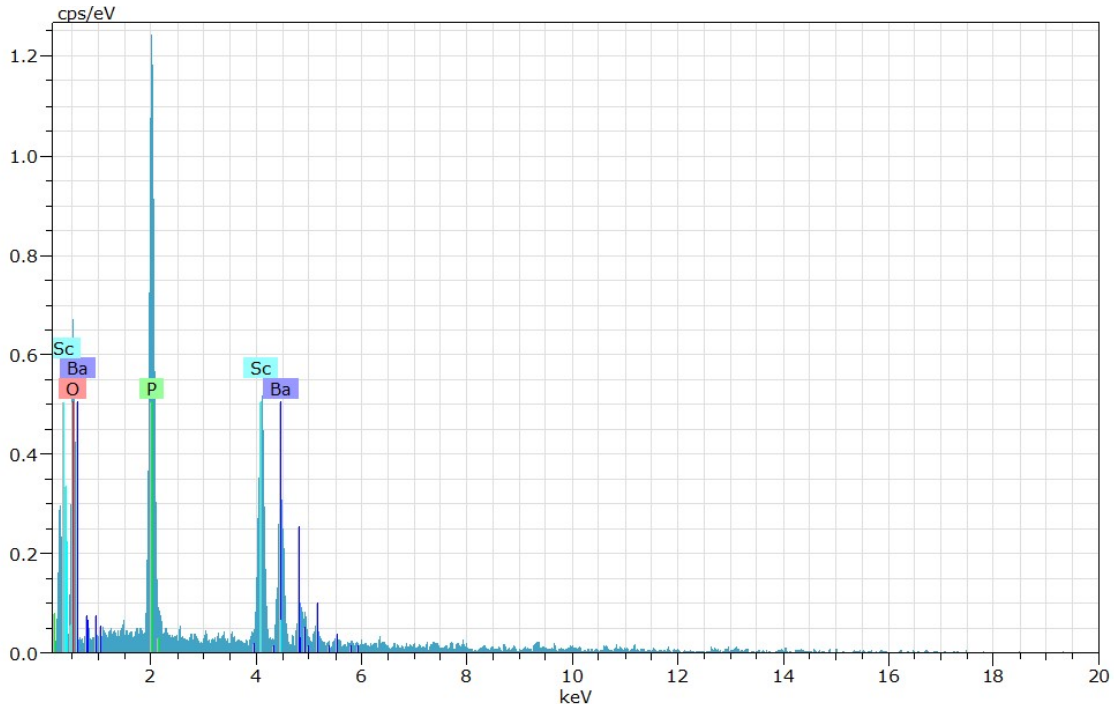

Figure S2. The EDS image and the quantitative analysis table of EDS for single-crystals of $BaSc_2(HPO_3)_4(H_2O)_2$.

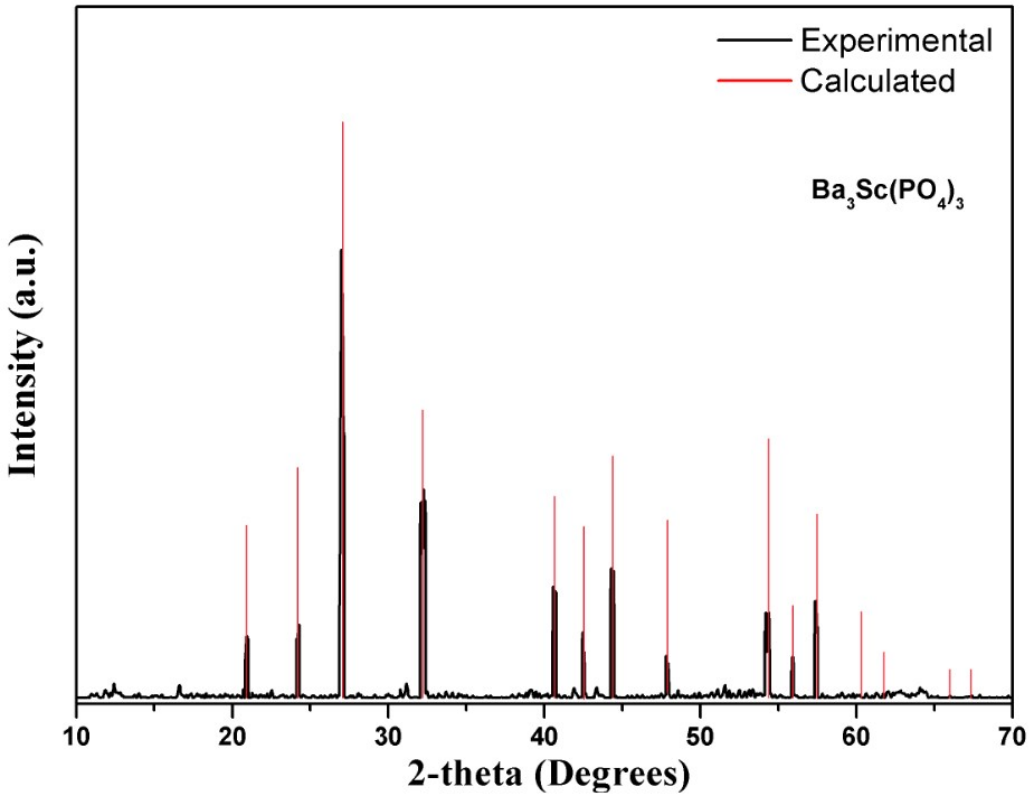

Figure S3. The PXRD of $BaSc_2(HPO_3)_4(H_2O)_2$ heated to 1000 °C.