Supporting Information

Hybridization-Activated New Deep Ultraviolet Transparent Nonlinear Optical Material $Ba_{11}[Al(PO_4)_4](P_2O_7)(PO_4)_3$ with Balanced Overall Performance and Parsimony-Forbidden Structure

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Experimental Details

Crystal Growth and High Temperature Solid State Synthesis of BAPO

Single crystals of BAPO were obtained by a spontaneous nucleation method. Stoichiometric raw materials of $BaCO_3$, Al_2O_3 and $NH_4H_2PO_4$ (99.9%, Aladdin Co.) were ground and blended into a φ40 platinum crucible, and followed by 7 days' holding at 1473.15 K with a crystal growing furnace. After a slow cooling to room temperature within one month, colourless crystals of BAPO were observed at the surface of the flux. Polycrystalline samples of BAPO were synthesized by traditional high temperature solid state reaction. Raw materials of $BaCO_3$, Al_2O_3 and $NH_4H_2PO_4$ in stoichiometric ratio with a total weight of 4g were grinded into micron-sized particles, blended into uniformity and placed into a corundum crucible. The mixture was held at 873.15 K for 2 days in a muffle furnace and followed by a uniform grinding. Then it was slowly heated to 1423.15 K within one day, and slowly cooled to room temperature at a rate of 400 K per day right after 7 days' holding.

Single Crystal and Powder X-ray Diffraction

A colorless crystal with dimensions of $0.1\times0.07\times0.05 mm^3$ was selected for single-crystal X-ray diffraction. The diffraction data were collected on an Agilent Technologies Super Nova Dual Wavelength CCD diffractometer equipped with graphite-monochromatic Mo Kα radiation (λ= 0.71073 Å) at 100.01 K and and data reduction was done by using CrysAlisPro software[1]. The crystal structure was solved by the direct methods and refined by full matrix least squares on F^2 by SHELXL-2015 program[2]. The structure was verified using the ADDSYM algorithm from the program PLATON[3], and no higher symmetry was found. The diffraction data of powder samples was collected by powder X-ray diffraction measurement on a Rigaku MiniFlex 600 X-ray diffractometer using Cu Kα radiation (λ= 1.5418Å) at room temperature in the angular range of 2θ = 5-70° with a scan step width of 0.02° and a scan rate of 2.5°/min.

UV-Vis diffuser reflectance

The reflection spectrum of LNTP crystal was performed with a PE Lambda 900 UV-vis-NIR spectrophotometer in the range of 200–1100 nm. The BaSO4 plate was used as a standard (100 % reflectance). The absorption spectrum was calculated from reflectance spectrum using the Kubelka-Munk function: $\alpha/S = (1-R)^2/2R$, where R is the absorption coefficient, S is the scattering coefficient, which is practically wavelength-independent when the particle size is larger than 5 μm, and R is the reflectance.[4]

IR spectrum

IR spectrum was recorded on a Magna 750 FT-IR spectrometer in the range of 4000-450 cm^{-1}.

Thermal Analysis

Thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) measurements were performed on a NETZSCH STA 449C apparatus using Al_2O_3 as reference material under N_2 flow with a sample heating rate of 10.0k/min from 50℃ to 1100℃. The crystal powders has melt at 1088℃, after the melting, the sample was checked by powder XRD.

Powder Second Harmonic Generation Measurement

SHG Measurements for BAPO were carried out with a Nd:YAG 1064 nm laser. Sieved KDP sample with particle size of 212-300 μm were taken as reference for assuming SHG signals. The samples were ground and sieved into six discrete ranges of particle sizes, namely 45-53, 53-75, 75-109, 109-150, 150-212 and 212-270 μm.

Energy Dispersive Spectrum

Microprobe elemental analyses for the Ba, Al and P elements were performed on a field-emission scanning electron microscope (FESEM, JSM6700F) equipped with an energy-dispersive X-ray spectroscope (EDS, Oxford INCA).

Figure S1. DSC and TG curves for BAPO in the temperature range of 700-1100℃.

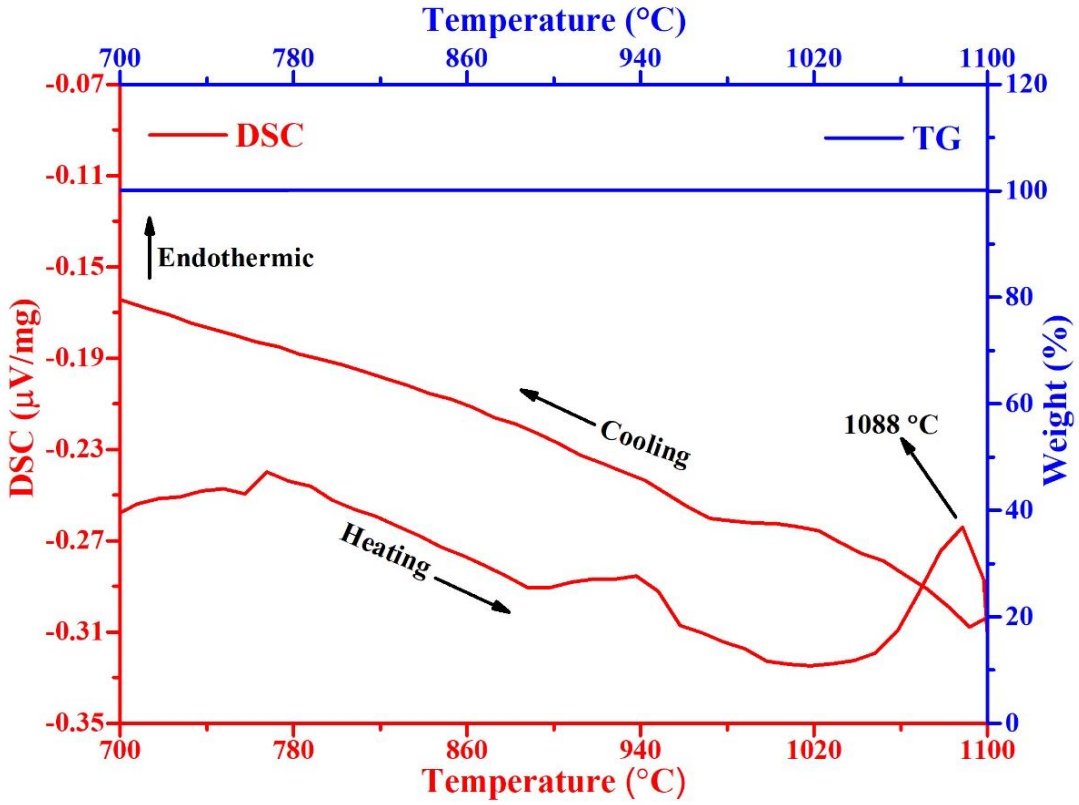

Figure S2. Experimental PXRD patterns for BAPO samples before- and after-DSC together with the calculated PXRD pattern for BAPO.

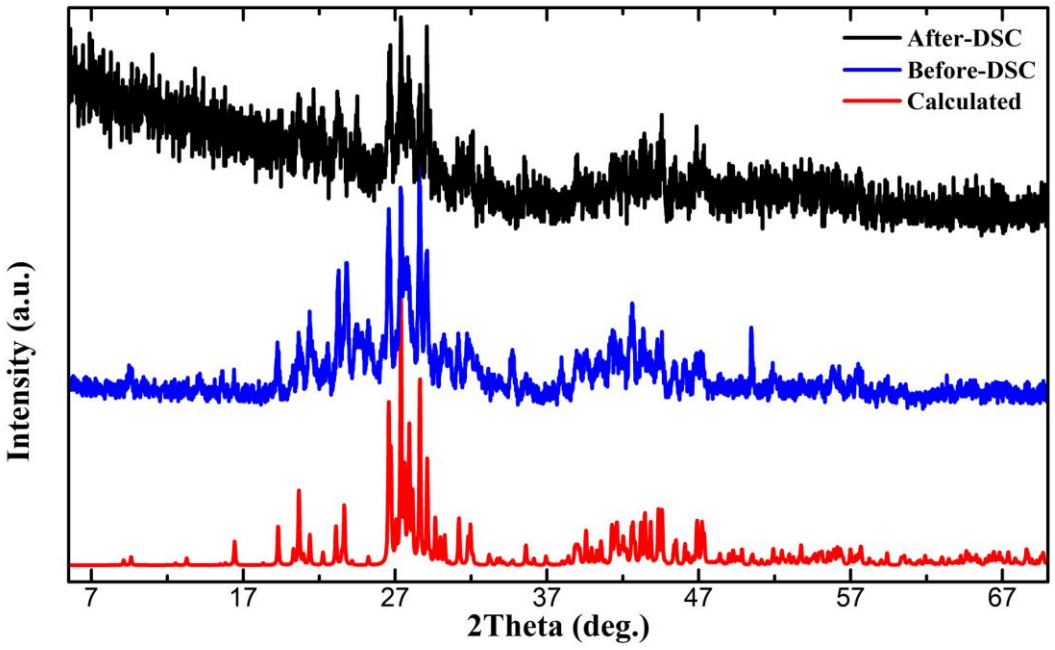

Figure S3. Energy Dispersive Spectrum for BAPO.

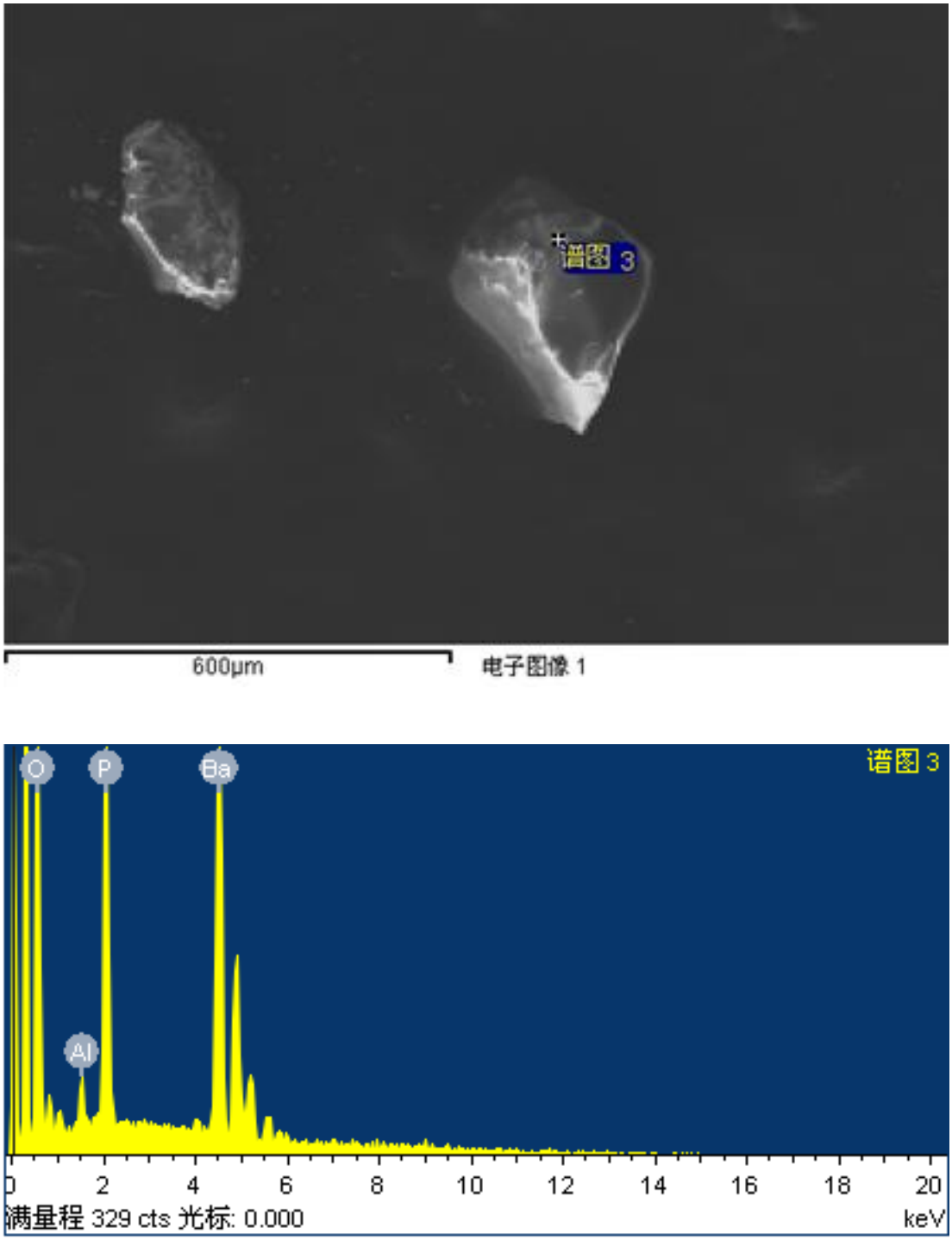

Figure S4. IR Spectrum for BAPO.

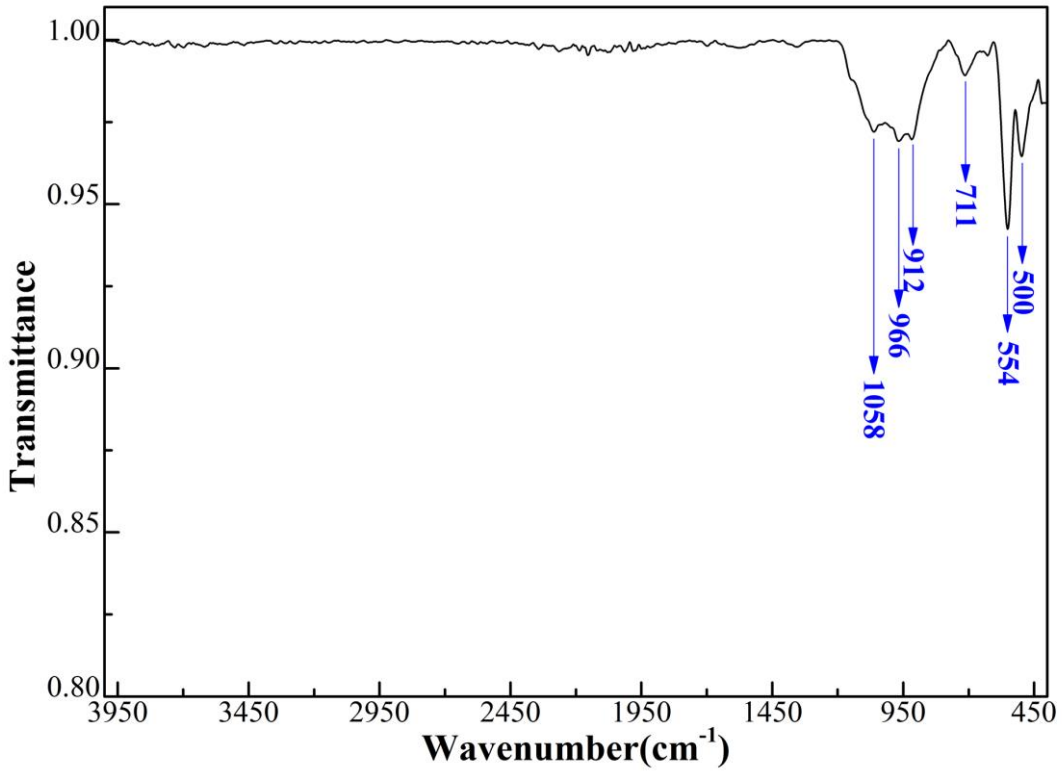

Figure S5. Energy Dispersive Spectrum showing the minute amount of Fe^{3+} in BAPO.

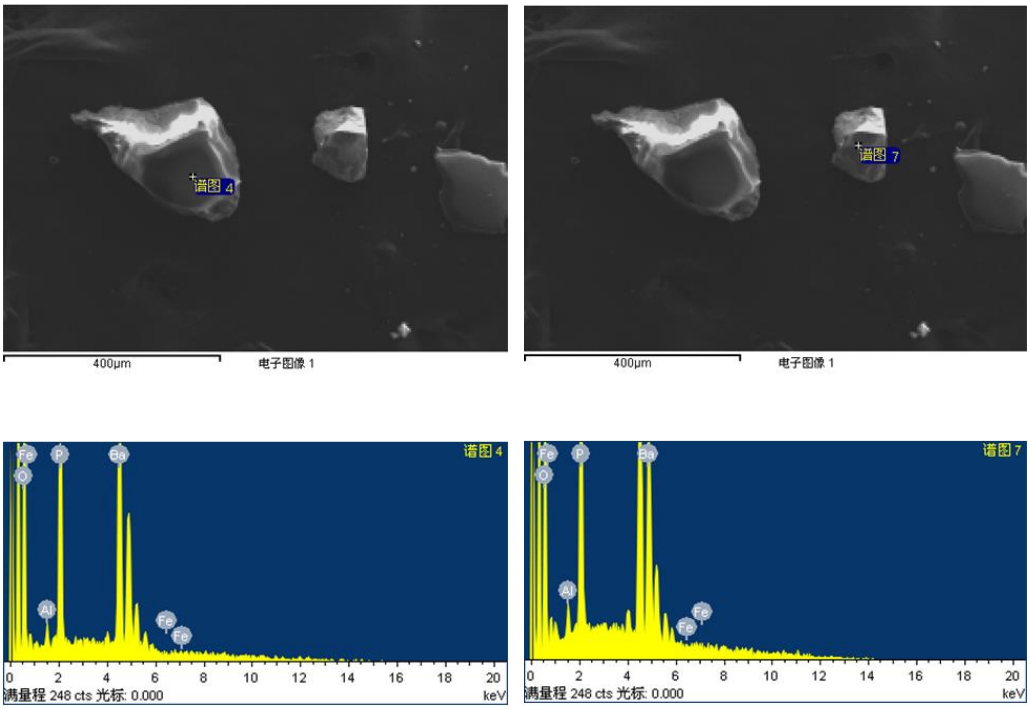

Table S1. Crystal data and structure refinement for BAPO.

Formula	Ba11AlP9O35
formula mass(amu)	2376.45
crystal system	othorhombic
space group	*Iba*2 (45)
a(Å)	13.3196(3)
b(Å)	14.1030(3)
c(Å)	18.3913(6)
α	90
β	90
γ	90
V(Å^3)	3454.75(15)
Z	4
T(K)	100.01
ρ*(calcd)(g/cm^3)*	4.569
λ (Å)	0.71073
F(000)	4176
θ*(deg)*	3.6340-28.8510
Cryst size (mm^3)	0.1×0.07×0.05
μ(mm^{-1})	12.876
R(F) [a]	0.0344
$R_W(F_o^2)$ [b]	0.0734

[a] $R(F) = \sum \big| \, |F_o| - |F_c| \, \big| / \sum |F_o|$ for $F_o^2 > 2\sigma(F_o^2)$.

[b] $R_w(F_o^2) = \{(\sum [w(F_o^2 - F_c^2)^2] / \sum wF_o^4\}^{1/2}$ for all data.

$w^{-1} = \sigma^2(F_o^2) + (zP)^2$, where $P = (_{Max}(F_o^2, 0) + 2F_c^2)/3$.

Table S2. Atomic coordinates and equivalent isotropic displacement parameters for BAPO.

Atom	Wyck.	Site	x/a	y/b	z/c
Ba1	8c	1	0.82535(6)	0.32236(5)	0.39052(6)
Ba2	8c	1	0.59261(7)	0.26358(6)	0.54590(5)
Ba3	8c	1	0.32883(7)	0.43793(7)	0.52353(5)
Ba4	8c	1	0.30393(6)	0.55949(6)	0.76122(5)
Ba5	8c	1	0.09356(7)	0.77715(6)	0.72442(6)
Ba6	4b	..2	0	1/2	0.70617(7)
Al1	4b	..2	0	1/2	0.9929(4)
O1	8c	1	0.6992(8)	0.1805(8)	0.4320(7)
O10	8c	1	0.1672(7)	0.6190(7)	0.6584(7)
O11	8c	1	-0.0617(8)	0.6827(7)	0.6771(7)
O12	8c	1	0.2405(11)	0.3450(11)	0.6396(7)
O13	8c	1	0.4544(18)	0.6688(16)	0.8196(15)
O14	8c	1	0.430(2)	0.6331(17)	0.8716(15)
O15	8c	1	0.4566(16)	0.5122(15)	0.8668(13)
O16	8c	1	0.6219(11)	0.6235(16)	0.8615(9)
O17	8c	1	0.2073(9)	0.2504(7)	0.7536(7)
O18	8c	1	0.1865(13)	0.5107(8)	0.9056(7)
O19	8c	1	0.0333(8)	0.6018(8)	0.9434(7)
O2	8c	1	0.5223(16)	0.4148(15)	0.4779(13)
O20	8c	1	0.0910(8)	0.4627(8)	1.0547(7)
O21	8c	1	0.1061(8)	0.6272(7)	0.8180(5)
O22	8c	1	0.1689(7)	0.4199(7)	0.7551(7)
O3	8c	1	0.486(2)	0.3547(17)	0.4485(13)
O4	8c	1	0.4981(16)	0.5859(15)	0.5990(13)
O5	8c	1	0.4174(15)	0.5658(15)	0.6337(13)
O6	8c	1	0.6030(15)	0.5447(14)	0.6568(13)
O7	8c	1	0.5229(15)	0.5457(13)	0.7295(13)
O8	8c	1	0.2533(8)	0.6153(7)	0.5333(7)
O9	8c	1	0.1038(8)	0.7182(7)	0.5521(7)
P1	8c	1	0.1555(4)	0.6276(4)	0.5757(2)
P2	4a	..2	1/2	1/2	0.6545(4)
P3	8c	1	0.5212(4)	0.6030(4)	0.8852(4)
P4	8c	1	0.1705(4)	0.3324(4)	0.7055(2)
P5	8c	1	0.1320(4)	0.6070(2)	0.8968(2)

Table S3. Anisotropic displacement parameters, in $Å^2$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba1	0.01660	0.00990	0.01080	-0.00510	-0.00020	0.00010
Ba2	0.01510	0.00910	0.01360	0.00080	0.00110	0.00120
Ba3	0.01620	0.01640	0.01160	0.00570	0.00050	-0.00080
Ba4	0.00710	0.01080	0.01940	-0.00190	0.00210	-0.00380
Ba5	0.01470	0.00860	0.02700	-0.00080	-0.00470	0.00020
Ba6	0.00720	0.00650	0.01760	0.00150	0.00000	0.00000
Al1	0.02000	0.01400	0.01200	0.00200	0.00000	0.00000
O1	0.01700	0.02200	0.01700	-0.01500	-0.00300	0.00200
O10	0.01500	0.01600	0.01400	0.00000	-0.00100	-0.00400
O11	0.02900	0.00800	0.01600	0.00100	0.01000	0.00000
O12	0.04600	0.06500	0.03500	0.04200	0.03100	0.03500
O13	0.02500	0.02000	0.04600	-0.00100	0.00600	0.01100
O14	0.03300	0.02400	0.04400	0.00700	0.00200	0.00400
O15	0.02000	0.01400	0.03600	-0.00100	-0.00300	0.00200
O16	0.01900	0.18000	0.06300	-0.01100	-0.01000	0.05500
O17	0.03200	0.01200	0.01500	0.00700	0.00200	0.00100
O18	0.07300	0.02200	0.02800	0.01700	-0.01900	-0.00600
O19	0.01300	0.03500	0.01600	-0.01000	0.00100	0.00300
O2	0.02000	0.01800	0.01400	0.00100	-0.00400	0.00400
O20	0.03100	0.02000	0.01300	0.01700	0.00000	0.00200
O21	0.02200	0.01400	0.01200	0.00100	-0.00100	0.00300
O22	0.01300	0.00700	0.02800	0.00100	-0.00500	-0.00500
O3	0.03200	0.03100	0.02000	0.01300	0.00400	0.00600
O4	0.01800	0.01500	0.03200	0.00300	0.01200	0.01400
O5	0.01600	0.01000	0.02500	-0.00500	0.00300	0.00300
O6	0.01400	0.00600	0.02100	0.00200	0.00400	-0.00100
O7	0.02100	0.01300	0.02200	-0.00100	-0.00400	-0.00600
O8	0.02700	0.01700	0.02500	-0.01000	0.01400	-0.00600
O9	0.02000	0.01900	0.02600	-0.00300	-0.00400	0.01700
P1	0.01250	0.01310	0.01300	-0.00600	0.00150	-0.00030
P2	0.00900	0.01400	0.01300	0.00400	0.00000	0.00000
P3	0.02800	0.03100	0.06900	-0.01500	0.02100	-0.03500
P4	0.01320	0.01220	0.01300	0.00780	0.00300	-0.00010
P5	0.01550	0.00640	0.01100	-0.00340	0.00030	0.00040

Table S4. Selected geometric information for BAPO.

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Ba1—O19^{ii}	3.124 (11)	Ba5—O7^{x}	2.671 (19)	Ba6—O20^{xii}	3.083 (11)
Ba1—O22^{i}	2.847 (11)	Ba5—O6^{x}	2.81 (2)	Ba6—O21^{xi}	3.074 (10)
Ba1—O8^{iii}	2.960 (12)	Ba5—O13^{x}	2.66 (2)	Ba6—O21	3.074 (10)
Ba1—O1	2.722 (10)	Ba6—O11	2.757 (10)	P5—O19	1.571 (11)
Ba1—O18^{i}	2.676 (12)	Ba6—O11^{xi}	2.757 (10)	P5—O21	1.517 (10)
Ba1—O17^{i}	2.750 (11)	Ba6—O10	2.924 (10)	P5—O1^{xiii}	1.515 (11)
Ba1—O16^{iv}	2.866 (16)	Ba6—O10^{xi}	2.924 (10)	P5—O18	1.548 (12)
Ba1—O14^{v}	3.03 (2)	Ba6—O22	2.673 (9)	P4—O12	1.540 (12)
Ba1—O13^{v}	3.06 (2)	Ba6—O22^{xi}	2.673 (9)	P4—O11^{xi}	1.555 (11)
Ba2—O19^{v}	3.064 (11)	Ba6—O20^{iv}	3.083 (11)	P4—O22	1.535 (10)
Ba3—O8	2.703 (11)	P4—O17	1.536 (11)	Ba2—O12^{vi}	3.033 (18)
Ba3—O1^{viii}	2.934 (11)	Al1—O19^{xi}	1.757 (12)	Ba2—O11^{vii}	2.701 (11)
Ba3—O18^{iv}	2.970 (13)	Al1—O19	1.757 (12)	Ba2—O8^{iii}	2.680 (11)
Ba3—O5	2.96 (2)	Al1—O20^{xi}	1.743 (11)	Ba2—O1	2.788 (11)
Ba3—O4^{iii}	2.71 (2)	Al1—O20	1.743 (11)	Ba2—O9^{vii}	2.695 (11)
Ba3—O6^{iii}	2.63 (2)	P3—O16	1.440 (16)	Ba2—O5^{iii}	2.90 (2)
Ba3—O2	2.73 (2)	P3—O15^{iii}	1.69 (2)	Ba2—O4^{iii}	2.63 (2)
Ba3—O2^{iii}	2.99 (2)	P3—O15	1.58 (2)	Ba2—O2	2.64 (2)
Ba3—O3	2.77 (2)	P3—O2^{xiv}	1.72 (2)	Ba2—O3	2.62 (2)
Ba3—O14^{iv}	3.26 (3)	P3—O3^{xiv}	1.39 (2)	Ba3—O12	2.767 (12)
Ba4—O10	2.756 (10)	P3—O14	1.31 (3)	Ba4—O14	2.83 (3)
Ba4—O22	2.668 (9)	P3—O13	1.76 (3)	Ba4—O13	2.75 (2)
Ba4—O21	2.991 (11)	P1—O10	1.533 (11)	Ba5—O12^{ix}	2.869 (14)
Ba4—O18	3.158 (15)	P1—O8	1.529 (11)	Ba5—O11	2.609 (11)
Ba4—O5	2.79 (2)	P1—O20^{iv}	1.584 (11)	Ba5—O10	2.723 (10)
Ba4—O17^{ix}	2.700 (10)	P1—O9	1.515 (11)	P2—O7	1.55 (2)
Ba4—O7	2.98 (2)	P2—O5^{iii}	1.49 (2)	P2—O7^{iii}	1.55 (2)
Ba4—O7^{iii}	2.80 (2)	P2—O5	1.49 (2)	P2—O6	1.51 (2)
Ba4—O6^{iii}	2.72 (2)	P2—O4	1.59 (2)	P2—O6^{iii}	1.51 (2)
Ba4—O15	2.89 (2)	P2—O4^{iii}	1.59 (2)	Ba5—O21	2.732 (10)

Symmetry codes: (i) −x+1, y, z−1/2; (ii) x+1, −y+1, z−1/2; (iii) −x+1, −y+1, z; (iv) x, −y+1, z−1/2; (v) x+1/2, y−1/2, z−1/2; (vi) x+1/2, −y+1/2, z; (vii) −x+1/2, y−1/2, z; (viii) x−1/2, −y+1/2, z; (ix) −x+1/2, y+1/2, z; (x) x−1/2, −y+3/2, z; (xi) −x, −y+1, z; (xii) −x, y, z−1/2; (xiii) x−1/2, y+1/2, z+1/2; (xiv) x, −y+1, z+1/2; (xv) −x+1, y, z+1/2; (xvi) x−1, −y+1, z+1/2; (xvii) x+1/2, −y+3/2, z; (xviii) −x, y, z+1/2.

Table S5. Calculated bond valence sum (BVS) for atoms in BAPO.

Atom	BVS
Ba1	1.76
Ba2	2.20
Ba3	1.52
Ba4	1.58
Ba5	2.19
Ba6	2.08
Al1	2.82
O1	-2.05
O10	-2.01
O11	-2.20
O12	-1.84
O13	-1.45
O14	-2.64
O15	-2.11
O16	-2.00
O17	-2.15
O18	-1.7
O19	-2.04
O2	-1.59
O20	-1.92
O21	-1.87
O22	-2.17
O3	-2.51
O4	-1.81
O5	-2.08
O6	-2.27
O7	-1.95
O8	-2.09
O9	-1.64
P1	4.91
P2	4.99
P3	5.34
P4	4.88
P5	4.94

Bond valence sums are calculated by using bond-valence theory ($S_i = \exp[(R_o - R_i)/B]$, where R_o is an empirical constant, R_i is the length of bond i (in angstroms), and B = 0.37).

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