Electronic Supplementary Information

for

Growth and theoretical study on the deep-ultraviolet transparent β-$CsBa_2(PO_3)_5$ nonlinear optical crystal

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1. Details of Characterization Experiments

Powder X-ray diffraction (PXRD) was carried out at room temperature on a Bruker D8 Advance diffractomerter using graphite monochromatized Cu Kα radiation. The PXRD data were collected in the 2θ range of 10–60°.

Infrared (IR) spectrum was recorded on a Nicolet Magna-IR 560 ESP Fourier transform IR (FTIR) spectrometer. A KBr pressed plate was employed for record.

Raman spectrum was measured on a Renishaw inVia Raman microscope. The wavelength of the excited CW argon laser was 514 nm.

High-temperature in-situ XRD analysis of β-CBPO polycrystalline sample were performed on the Bruker D8 advance diffractometer in a vacuum accessory in the range of 500°C–900°C. The PXRD patterns were recorded at 2θ = 10–60° with a delay time of 600 s before each pattern recording. The step size was 0.0205°, and the step time was 0.24 s during the whole analysis. After that, the sample was cooled to room temperature, and the PXRD pattern was recorded again.

2. Single X-ray Diffraction Information and Data Tables

Single crystal X-ray diffraction data for β-$CsBa_2(PO_3)_5$ crystal was collected on an Agilent Gemini E diffractometer equipped with an Eos CCD detector and an Cryojet XL liquid nitrogen cryogenic system. Mo Kα confocal monochromated radiation (λ = 0.71073 Å) was used. Intensity data were corrected for Lorentz, polarization, and background effects using the Agilent program CrysAlisPro, and a semi-empirical correction for adsorption was applied. SHELXS-97 and SHELXL-97 programs were used for the solution and refinement of the crystal structure, respectively. All non-hydrogen atoms were refined anisotropically.

Crystal data, data collection, and refinement parameters are summarized in Table S1. The fractional atomic coordinates and the equivalent isotropic displacement parameters are listed in Table S2. The anisotropic displacement parameters are given in Table S3.

Table S1. Crystal data, data collection, and refinement parameters for β-$CsBa_2(PO_3)_5$.

Empirical formula	$CsBa_2(PO_3)_5$
Formula weight	802.44
Temperature / K	103.8
Crystal system	monoclinic
Space group	*Pn*
a / Å, *b* / Å, *c* / Å	8.7687(3), 7.3223(3), 10.9901(5)
α/°, β/°, γ/°	90.00, 90.224(3), 90.00
Volume / Å^3	705.63(5)
Z	2
ρ_{calc} / mg·mm^{-3}	3.777
μ / mm^{-1}	8.735
$F_{(000)}$	724
Crystal size / mm^3	0.50 × 0.18 × 0.04
2θ range for data collection	5.94 to 51.96°
Index ranges	$-10 \le h \le 10$, $-9 \le k \le 9$, $-13 \le l \le 9$
Reflections collected	4994
Independent reflections	2187 [R_{int} = 0.0345 (inf - 0.9 Å)]
Data/restraints/parameters	2187/14/209
Goodness-of-fit on F^2	1.054
Final *R* indexes [$I>2\sigma(I)$]	R_1 = 0.0291, wR_2 = 0.0715
Final *R* indexes [all data]	R_1 = 0.0295, wR_2 = 0.0718
Largest diff. peak/hole / e·Å^{-3}	1.337/−1.083
Flack Parameters	−0.03(2)
Completeness	0.999

Table S2. The fractional atomic coordinates ($\times 10^4$) and the equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for β-$CsBa_2(PO_3)_5$. (U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.)

Atom	*x*	*y*	*z*	U_{eq}
Cs1	98.6(6)	3590.2(8)	3223.4(6)	9.06(19)
Ba1	1994.6(6)	1556.3(7)	7058.6(5)	7.18(17)
Ba2	-2930.6(7)	1294.4(6)	6172.2(6)	6.94(17)
P1	-1223(3)	-3493(3)	6109(3)	7.6(6)
P2	246(3)	-1139(3)	4351(2)	6.7(5)
P3	3664(3)	-1545(3)	4466(3)	6.7(6)
P4	3879(3)	-5515(3)	5128(2)	7.1(5)
P5	5946(3)	-6558(3)	3132(3)	7.4(5)
O1	-2502(7)	-2300(9)	6498(6)	9.5(15)
O2	-1388(8)	-5505(9)	6086(6)	13.5(15)
O3	304(7)	-2879(9)	6806(6)	7.8(13)
O4	-762(7)	-2858(8)	4751(6)	8.3(13)
O5	72(7)	385(8)	5243(6)	8.2(14)
O6	-109(7)	-751(9)	3045(6)	8.7(14)
O7	1877(7)	-2034(9)	4421(7)	15.0(16)
O8	3968(7)	-84(9)	5365(6)	11.6(14)
O9	4203(8)	-1374(8)	3183(7)	10.0(15)
O10	4309(9)	-3399(8)	5054(7)	7.3(16)
O11	2233(7)	-5848(9)	5252(6)	8.3(14)
O12	4903(9)	-6272(8)	6079(7)	13.9(16)
O13	4347(9)	-6249(8)	3813(7)	11.8(16)
O14	6813(7)	-4824(8)	3093(6)	10.1(14)
O15	6759(8)	-8198(9)	3628(7)	11.2(15)

Table S3. The anisotropic displacement parameters ($Å^2 \times 10^3$) for β-$CsBa_2(PO_3)_5$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cs1	10.6(4)	10.5(3)	6.0(3)	0.7(2)	-1.4(3)	0.8(2)
Ba1	8.6(3)	9.3(3)	3.6(3)	-0.6(2)	-1.0(2)	0.0(2)
Ba2	8.6(3)	7.9(3)	4.3(3)	0.2(2)	-0.7(2)	0.5(2)
P1	9.7(14)	9.7(13)	3.5(14)	0.3(9)	-1.3(11)	-0.5(9)
P2	7.3(12)	9.1(11)	3.6(13)	0.4(9)	-1.4(10)	0.4(9)
P3	8.7(14)	8.1(12)	3.2(14)	1.7(9)	0.6(11)	1.3(9)
P4	10.2(12)	6.8(11)	4.5(12)	0.5(10)	0.2(9)	1.5(9)
P5	7.3(13)	9.9(11)	4.9(14)	0.6(9)	-1.1(10)	0.3(8)
O1	6(3)	12(3)	11(4)	2(3)	-2(3)	7(2)
O2	15(4)	12(3)	14(4)	6(3)	1(3)	-4(3)
O3	6(3)	11(3)	7(4)	1(3)	-2(3)	-2(3)
O4	11(3)	9(3)	5(3)	2(3)	-3(3)	-1(3)
O5	10(3)	8(3)	6(4)	-2(3)	-6(3)	0(2)
O6	12(3)	11(3)	3(3)	-1(2)	-5(2)	-1(2)
O7	7(4)	11(3)	27(5)	2(3)	1(3)	3(3)
O8	16(4)	7(3)	11(4)	-1(3)	-3(3)	4(3)
O9	11(4)	15(4)	4(4)	-1(3)	1(3)	2(2)
O10	6(4)	10(3)	5(4)	3(2)	-4(3)	-1(2)
O11	8(3)	12(3)	5(3)	4(2)	0(2)	-1(2)
O12	17(4)	13(4)	11(4)	-4(3)	-2(3)	0(3)
O13	18(4)	12(3)	6(4)	-2(3)	4(3)	-1(3)
O14	12(3)	10(3)	8(4)	-1(3)	0(3)	-2(3)
O15	9(4)	14(3)	11(4)	1(3)	0(3)	3(3)