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New Polymorphism for $BaTi(IO_3)_6$ with Two Polymorphs Crystallizing in the Same Space Group

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CONTENTS

Experimental Section

Caution: Hydrofluoric acid is toxic and corrosive! It must be handled with extreme caution and the appropriate protective equipment and training.

Materials

$BaCl_2\cdot 2H_2O$ (Tianjin Fu Chen Chemical Co., Ltd., 99.5%), TiO_2 (Tianjin Fu Chen Chemical Co., Ltd., 99%), HIO_3 (Alfa Aesar, 99.5%), HF (Tianjin Fu Chen Chemical Co., Ltd., 40%) were used as received.

Hydrothermal Syntheses

α- and β-$BaTi(IO_3)_6$ were both synthesized by the hydrothermal methods with the same starting materials and the same temperature program. The difference is that β-$BaTi(IO_3)_6$ was synthesized without mineralizers whereas α-$BaTi(IO_3)_6$ was synthesized with 0.5 ml HF as the mineralizer. For α- and β-$BaTi(IO_3)_6$, 0.200 g (0.82×10^{-3} mol) of $BaCl_2\cdot 2H_2O$, 0.200 g (2.50×10^{-3} mol) of TiO_2, 1.400 g (7.96×10^{-2} mol) of HIO_3 were combined with 5ml H_2O, and 0.5 ml HF were combined with 5 mL of H_2O to α-$BaTi(IO_3)_6$. The solutions were placed in 23-mL Teflon-lined autoclaves and subsequently sealed. The autoclaves were gradually heated to 220 °C, hold for 3 d, and cooled slowly to room temperature at a rate of 5 °C/h. The mother liquor was decanted from the products. The products were recovered by filtration and washed with water. The white stripe crystals were found in 90% and 85% yield for α- and β-$BaTi(IO_3)_6$ based on $BaCl_2\cdot 2H_2O$, respectively.

Crystallographic Determination

Two transparent colorless bulk single crystals of α- and β-$BaTi(IO_3)_6$ with dimensions of 0.065 x 0.086 x 0.102 and 0.061 x 0.078 x 0.097 mm^3 were selected for the single-crystal structural determination. The diffraction data collection was carried out on a Bruker D8 VENTURE CMOS X-ray source with Mo Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K. Data collection and reduction were performed using the APEX Ⅱ software, and absorption corrections were acquired based on a multiscan-type model.[1] The crystal structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using the SHELXTL-97 software package.[2] All nonhydrogen atoms were refined with the anisotropic displacement parameters. The absolute structure was examined for missing symmetry elements using PLATON,[3] and none were found.

Crystal data and structural refinement information for α- and β-$BaTi(IO_3)_6$ are summarized in Table S1. Atomic coordinates and equivalent isotropic displacement parameters as well as calculated bond valence sums (BVS) for α- and β-$BaTi(IO_3)_6$ are collected in Table S2. Selected bond distances are given in Table S3.

Powder X-ray Diffraction

The phase purity of α- and β-$BaTi(IO_3)_6$ were confirmed by using powder X-ray diffraction (PXRD). This study was performed at room temperature on a SmartLab9KW X-ray diffractometer at room temperature (Cu-Kα radiation). Data was collected in the 2θ range of 10-70° with a step size of 0.01° and a step time of 2 s. As seen in Figure 1, the polycrystalline XRD pattern of title compound is in good agreement with the calculated.

Infrared Spectroscopy

The infrared spectra of α- and β-$BaTi(IO_3)_6$ were recorded on a Nicolet iS50 FT-IR spectrometer in the range 500-3500 cm^{-1}. The sample of ~10 mg was placed on the test platform for testing.

The UV-vis-NIR Diffuse Reflectance Spectra

The diffuse reflectance spectra of the α- and β-$BaTi(IO_3)_6$ powder samples were measured with a Shimadzu SolidSpec-3700DUV UV/Vis/NIR Spectrophotometer at room temperature in the measurement range from 240 to 2000 nm. Barium sulfate was used as a diffuse reflectance standard.

Thermal Analysis

The thermal analyses were carried out on NETZSCH STA 449C thermal analyzer instrument in an atmosphere of flowing N_2. The measurement temperatures range from 30 to 800 °C for α- and β-$BaTi(IO_3)_6$. The heating and cooling rate are 5 °C/min.

Reference

1. R. H. Blessing, *Acta Crystallographica Section A.,* 1995, **51**, 33.
2. G. M. Sheldrick, SHELXS-97: *Program for the Solution of Crystal Structures*, University of Göttingen: Germany, 1997.
3. A. L. Spek, Single-crystal Structure Validation with the Program PLATON, *J. Appl. Crystallogr.,* 2003, **36**, 7.

Table S1. Crystal data and structure refinement for α- and β-BaTi(IO$_3$)$_6$.

Empirical formula	α-BaTi(IO$_3$)$_6$	β-BaTi(IO$_3$)$_6$
Formula weight	1234.64 g/mol	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
space group	R-3c	
Unit cell dimensions	a = 10.9589(7) Å, c = 11.1331(10) Å,	a = 11.4412(17) Å, c = 11.1418(17) Å,
Z, Volume	1, 1157.93(18) Å^3	3, 1263.1(4) Å^3
Density (g/cm^3)	5.312	5.177
Absorption coefficient (mm^{-1})	15.150	18.310
F (000)	1620	1668
Theta range for data collection	2.82 to 27.49°	2.75 to 27.50°
Limiting indices	$-14 \leq h \leq 9$ $-11 \leq k \leq 14$ $-14 \leq l \leq 14$	$-14 \leq h \leq 14$ $-14 \leq k \leq 14$ $-14 \leq l \leq 14$
Reflections collected	2964	9462
Completeness to theta	100 %	100 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	601 / 0 / 41	646 / 0 / 42
Goodness-of-fit on F^2	0.712	1.038
Final R indices [F_o^2>2s(F_o^2)][a]	R_1 = 0.0232, wR_2 = 0.0751	R_1 = 0.0258, wR_2 = 0.1145
R indices (all data)	R_1 = 0.0261, wR_2 = 0.0824	R_1 = 0.0287, wR_2 = 0.1187
Largest diff. peak and hole (e·Å^{-3})	1.016 and −2.575	1.372 and −1.741

[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. Crystal data and structure refinement for α- and β-BaTi(IO$_3$)$_6$ at low temperature.

Empirical formula	α-BaTi(IO$_3$)$_6$	β-BaTi(IO$_3$)$_6$
Formula weight	1234.64 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
space group	R-3c	
Unit cell dimensions	a = 10.9180(5) Å, c = 11.0808(6) Å,	a = 11.3909(6) Å, c = 11.1056(7) Å,
Z, Volume	3, 1143.90(12) Å^3	3, 1247.93(15) Å^3
Density (g/cm^3)	5.377	4.929
Absorption coefficient (mm^{-1})	15.336	14.057
F (000)	1620	1620
Theta range for data collection	2.832 to 27.471°	2.762 to 27.454°
Limiting indices	$-12 \leq h \leq 13$ $-14 \leq k \leq 13$ $-14 \leq k \leq 14$	$-14 \leq h \leq 14$ $-14 \leq k \leq 14$ $-14 \leq l \leq 14$
Reflections collected	3924	4208
Completeness to theta	100 %	100 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	584 / 0 / 31	641 / 0 / 42
Goodness-of-fit on F^2	0.746	1.156
Final R indices [F_o^2>2s(F_o^2)][a]	R_1 = 0.0179, wR_2 = 0.0773	R_1 = 0.0317, wR_2 = 0.1348
R indices (all data)	R_1 = 0.0212, wR_2 = 0.0871	R_1 = 0.0342, wR_2 = 0.1373
Largest diff. peak and hole (e·Å^{-3})	0.859 and −1.031	3.285 and −2.689

[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 S3a. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for α-$BaTi(IO_3)_6$ U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}	BVS
Ba1	0	0	0.5	10(2)	2.462
Ti1	3333	6666	6666	11(5)	4.173
I1	1146(3)	4079(3)	4557(3)	10(2)	5.011
O1	1681(4)	5521(4)	5675(3)	12(7)	2.167
O2	1271(4)	2875(4)	5550(3)	15(8)	2.084
O3	2740(4)	4702(4)	3690(4)	17(8)	1.871

Table S3b. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for β-$BaTi(IO_3)_6$ U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}	BVS
Ba1	0	0	0.38009(19)	0.0234(4)	2.21
Ti1	0.333333	0.666667	0.666667	0.0134(7)	4.355
I1	0.07188(4)	0.35479(4)	0.55802(4)	0.0118(3)	4.988
O1	0.0956(6)	0.2878(6)	0.6972(5)	0.0242(12)	1.823
O2	0.1224(5)	0.2718(6)	0.4524(5)	0.0182(11)	2.132
O3	0.2379(5)	0.5135(5)	0.5609(6)	0.0206(12)	2.202

Table S4a. Selected bond distances (Å) and angles (deg) for α-BaTi(IO$_3$)$_6$.

Ba1-O2	2.802(4)	O2-Ba1-O3	124.38(10)
Ba1-O2	2.802(4)	O2-Ba1-O3	124.38(10)
Ba1-O2	2.802(4)	O2-Ba1-O3	117.19(10)
Ba1-O2	2.802(4)	O2-Ba1-O3	66.90(10)
Ba1-O2	2.802(4)	O2-Ba1-O3	55.62(10)
Ba1-O2	2.802(4)	O2-Ba1-O3	62.81(10)
Ba1-O3	2.955(4)	O2-Ba1-O3	113.10(10)
Ba1-O3	2.955(4)	O3-Ba1-O3	180
Ba1-O3	2.955(4)	O2-Ba1-O3	66.90(10)
Ba1-O3	2.955(4)	O2-Ba1-O3	124.38(10)
Ba1-O3	2.955(4)	O2-Ba1-O3	62.81(10)
Ba1-O3	2.955(4)	O3-Ba1-O3	111.82(12)
Ti1-O1	1.950(3)	O2-Ba1-O3	113.10(10)
Ti1-O1	1.950(3)	O2-Ba1-O3	55.62(10)
Ti1-O1	1.950(4)	O2-Ba1-O3	117.19(10)
Ti1-O1	1.950(4)	O3-Ba1-O3	68.18(12)
Ti1-O1	1.950(3)	O2-Ba1-O3	62.81(10)
I1-O1	1.860(4)	O2-Ba1-O3	66.90(10)
I1-O2	1.779(3)	O2-Ba1-O3	55.62(10)
I1-O3	1.805(4)	O3-Ba1-O3	111.82(12)
O2-Ba1-O2	180	O3-Ba1-O3	111.82(12)
O2-Ba1-O2	115.36(5)	O2-Ba1-O3	62.81(10)
O2-Ba1-O2	64.64(5)	O2-Ba1-O3	66.90(10)
O2-Ba1-O2	64.64(5)	O2-Ba1-O3	55.62(10)
O2-Ba1-O2	115.36(5)	O3-Ba1-O3	68.18(12)
O2-Ba1-O2	115.36(5)	O3-Ba1-O3	68.18(12)
O2-Ba1-O2	64.64(5)	O3-Ba1-O3	68.18(12)
O2-Ba1-O2	180.00(14)	O3-Ba1-O3	68.18(12)

O2-Ba1-O2	64.64(5)	O2-Ba1-O3	117.19(10)
O2-Ba1-O2	115.36(5)	O2-Ba1-O3	113.10(10)
O2-Ba1-O2	180	O2-Ba1-O3	124.38(10)
O2-Ba1-O2	115.36(5)	O3-Ba1-O3	111.82(12)
O2-Ba1-O2	64.64(5)	O3-Ba1-O3	111.82(12)
O2-Ba1-O2	64.64(5)	O3-Ba1-O3	180
O2-Ba1-O2	115.36(5)	O2-I1-O3	101.18(17)
O2-Ba1-O3	55.62(10)	O3-I1-O1	101.67(16)
O2-Ba1-O3	62.81(10)	O2-I1-O1	96.12(16)
O2-Ba1-O3	113.10(10)	O1-Ti1-O1	91.08(14)
O2-Ba1-O3	124.38(10)	O1-Ti1-O1	88.93(14)
O2-Ba1-O3	117.19(10)	O1-Ti1-O1	88.93(14)
O2-Ba1-O3	66.90(10)	O1-Ti1-O1	91.08(14)
O2-Ba1-O3	113.10(10)	O1-Ti1-O1	91.08(14)
O2-Ba1-O3	55.62(10)	O1-Ti1-O1	88.92(14)
O2-Ba1-O3	117.19(10)	O1-Ti1-O1	180
O3-Ba1-O3	68.18(12)	O1-Ti1-O1	180
O2-Ba1-O3	66.90(10)	O1-Ti1-O1	88.92(14)
O2-Ba1-O3	124.38(10)	O1-Ti1-O1	91.08(14)
O2-Ba1-O3	62.81(10)	O1-Ti1-O1	88.92(14)
O3-Ba1-O3	111.82(12)	O1-Ti1-O1	180
O3-Ba1-O3	180	O1-Ti1-O1	91.08(14)
O2-Ba1-O3	117.19(10)	O1-Ti1-O1	91.07(14)
O2-Ba1-O3	113.10(10)	O1-Ti1-O1	88.92(14)

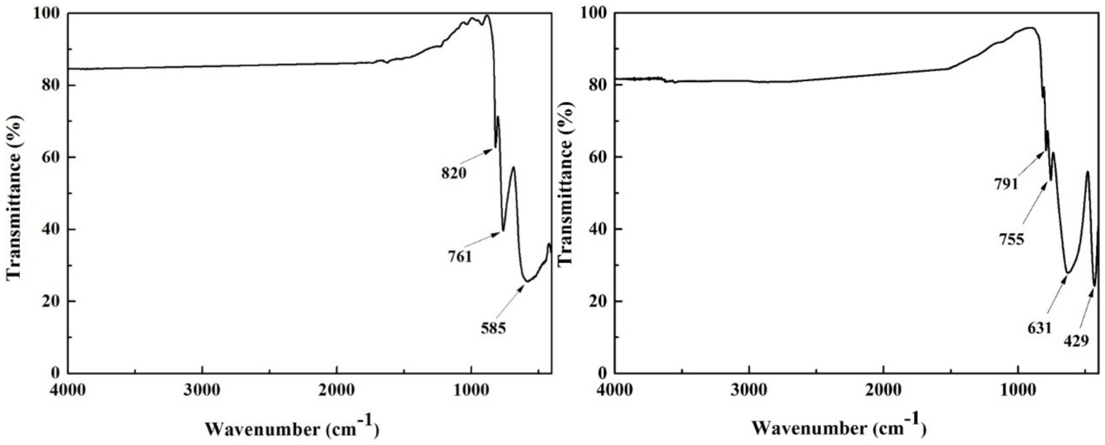
Table S4b. Selected bond distances (Å) and angles (deg) for *β*-$BaTi(IO_3)_6$.

Ba1-O1	3.031(5)	O2-Ba1-O2	112.05(9)
Ba1-O1	3.031(5)	O2-Ba1-O1	172.64(13)
Ba1-O1	3.031(5)	O2-Ba1-O1	61.31(13)
Ba1-O2	3.268(5)	O2-Ba1-O1	61.31(13)
Ba1-O2	3.268(5)	O2-Ba1-O1	74.47(13)
Ba1-O2	3.268(5)	O2-Ba1-O1	61.31(13)
Ba1-O2	2.805(5)	O1-Ba1-O1	112.37(8)
Ba1-O2	2.805(5)	O2-Ba1-O2	128.52(10)
Ba1-O2	2.805(5)	O1-Ba1-O2	117.41(12)
Ti1-O3	1.939(4)	O1-Ba1-O2	129.98(12)
Ti1-O3	1.939(4)	O2-Ba1-O2	56.10(5)
Ti1-O3	1.939(4)	O2-Ba1-O2	128.52(10)
Ti1-O3	1.939(4)	O1-Ba1-O2	117.41(12)
Ti1-O3	1.939(4)	O2-Ba1-O2	90.75(12)
Ti1-O3	1.939(4)	O2-Ba1-O2	128.52(10)
I1-O1	1.804(5)	O2-Ba1-O2	56.10(5)
I1-O2	1.788(4)	O1-Ba1-O2	129.98(12)
I1-O3	1.857(5)	O2-Ba1-O2	90.75(12)
O2-Ba1-O2	112.05(9)	O3-Ti1-O3	180
O2-Ba1-O2	112.05(9)	O3-Ti1-O3	86.8(2)
O2-Ba1-O1	74.47(13)	O3-Ti1-O3	86.8(2)
O2-Ba1-O1	172.64(13)	O3-Ti1-O3	86.8(2)
O1-Ba1-O1	112.37(8)	O3-Ti1-O3	93.2(2)
O2-Ba1-O1	74.47(13)	O3-Ti1-O3	86.8(2)
O2-Ba1-O1	172.64(13)	O3-Ti1-O3	180
O1-Ba1-O1	112.37(8)	O3-Ti1-O3	86.8(2)
O2-Ba1-O2	56.10(5)	O3-Ti1-O3	93.2(2)
O2-Ba1-O2	56.10(5)	O3-Ti1-O3	93.2(2)

O1-Ba1-O2	51.63(12)	O3-Ti1-O3	86.8(2)
O2-Ba1-O2	56.10(5)	O3-Ti1-O3	93.2(2)
O1-Ba1-O2	129.98(12)	O3-Ti1-O3	180
O1-Ba1-O2	51.63(12)	O3-Ti1-O3	93.2(2)
O2-Ba1-O2	56.10(5)	O3-Ti1-O3	93.2(2)
O1-Ba1-O2	51.63(12)	O2-I1-O1	100.0(2)
O1-Ba1-O2	117.41(12)	O1-I1-O3	95.6(2)
O2-Ba1-O2	90.75(12)	O2-I1-O3	94.9(2)

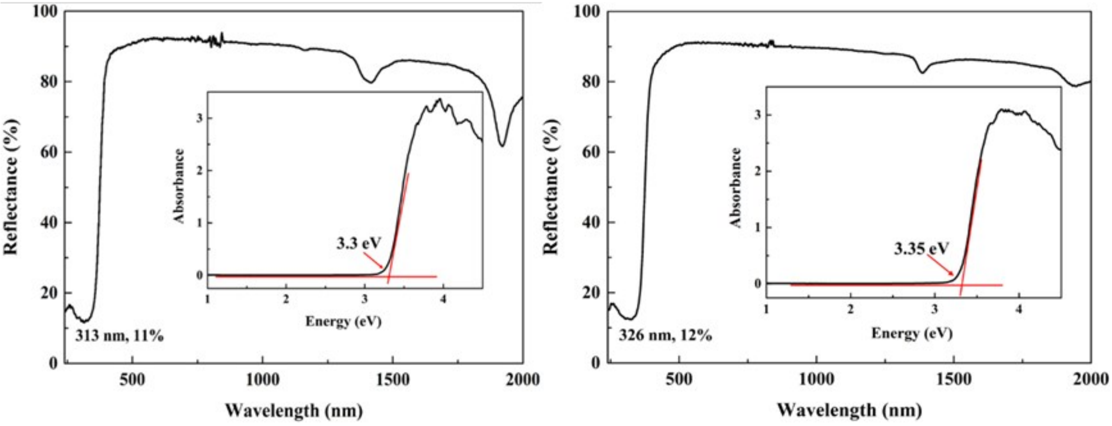
Table S5. The Ba^{2+} cations coordinated and Ba-O bonds in α- and β-$BaTi(IO_3)_6$.

α-$BaTi(IO_3)_6$		β-$BaTi(IO_3)_6$	
Ba1-O2	2.802(4) Å	Ba1-O1	3.031(5) Å
Ba1-O2	2.802(4) Å	Ba1-O1	3.031(5) Å
Ba1-O2	2.802(4) Å	Ba1-O1	3.031(5) Å
Ba1-O2	2.802(4) Å	Ba1-O2	3.268(5) Å
Ba1-O2	2.802(4) Å	Ba1-O2	3.268(5) Å
Ba1-O2	2.802(4) Å	Ba1-O2	3.268(5) Å
Ba1-O3	2.955(4) Å	Ba1-O2	2.805(5) Å
Ba1-O3	2.955(4) Å	Ba1-O2	2.805(5) Å
Ba1-O3	2.955(4) Å	Ba1-O2	2.805(5) Å
Ba1-O3	2.955(4) Å		
Ba1-O3	2.955(4) Å		
Ba1-O3	2.955(4) Å		
(Ba) – (O) $_{average}$	2.878 Å	(Ba) – (O) $_{average}$	3.035 Å



(a) (b)

Figure S1. IR spectra for (a) α- and (b) β-BaTi(IO$_3$)$_6$.



(a) (b)

Figure S2. The UV-Vis-NIR diffuse reflectance spectra for (a) *α*- and (b) *β*-BaTi$(IO_3)_6$.

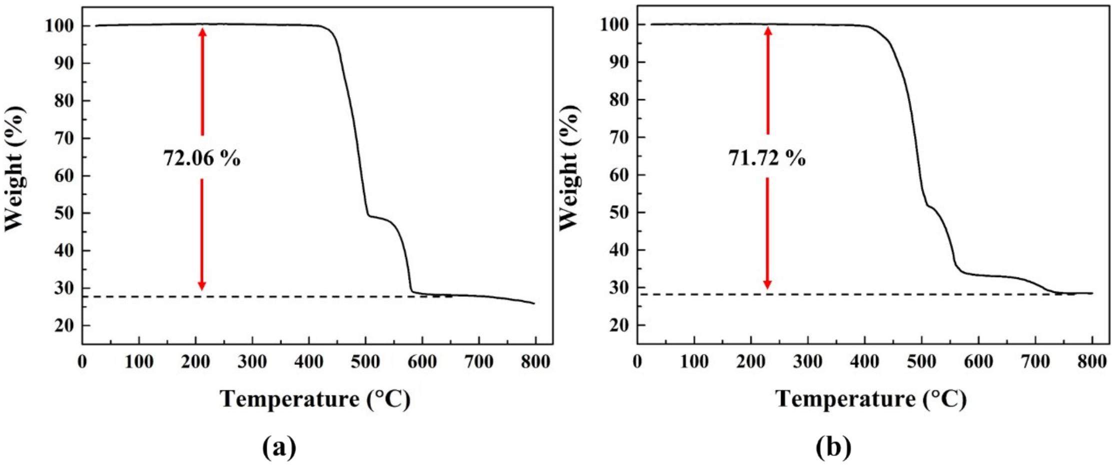


Figure S3. Thermogravimetric analysis diagram for (a) α- and (b) β-$BaTi(IO_3)_6$.

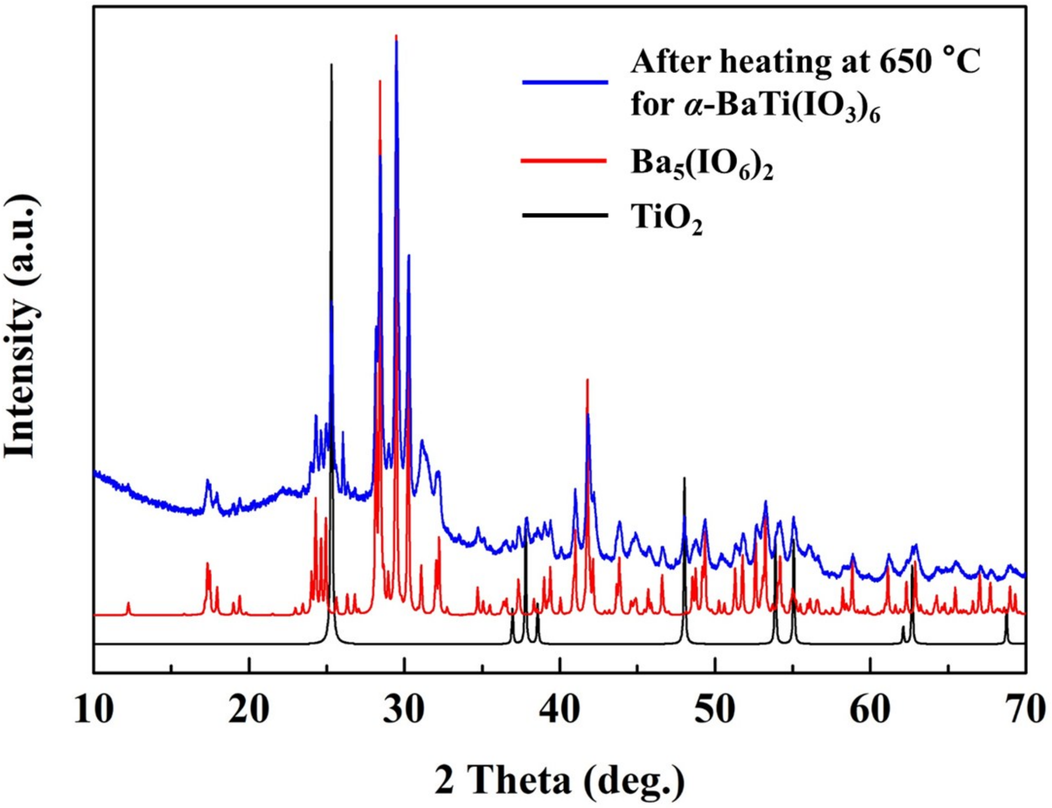


Figure S4. α-BaTi$(IO_3)_6$ decomposes above 650 °C to a mixture of $Ba_5(IO_6)_2$ and TiO_2.