Synthesis, Structure, and Characterization of d^0 Transition Metal Iodate: $BaTi(IO_3)_6 \cdot 0.5H_2O$

Zhen Qian,[a] Hongping Wu,[a] Hongwei Yu,[a*] Zhanggui Hu,[a] Jiyang Wang,[a] and Yicheng Wu[a]

[a]*Tianjin Key Laboratory of Functional Crystal Materials, Institute of Functional Crystal, Tianjin University of Technology, Tianjin 300384, China.*

To whom correspondence should be addressed. E-mail: hwyu15@gmail.com (Hongwei Yu).

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Table S1. Crystal data and structure refinement for $BaTi(IO_3)_6 \cdot 0.5H_2O$.

Empirical formula	$BaTi(IO_3)_6 \cdot 0.5H_2O$
Formula weight	1243.62 g/mol
Temperature	295(2) K
Wavelength	0.71073 Å
Crystal system	Trigonal
space group	*R*3
Unit cell dimensions	a = 11.1920(12) Å, c = 24.006(3) Å,
Z, Volume	1, 2604.1(7) $Å^3$
Density (g/cm^3)	4.758
Absorption coefficient (mm^{-1})	13.477
F (000)	3270
Theta range for data collection	2.266 to 27.535°
Limiting indices	−14 <= h <= 12 −13 <= k <= 10 −30 <= l <= 31
Reflections collected	6522
Completeness to theta	100.0 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2656 / 1 / 160
Goodness-of-fit on F^2	0.714
Final *R* indices [F_o^2>2s(F_o^2)][a]	R_1 = 0.0291, wR_2 = 0.0867
R indices (all data)	R_1 = 0.0342, wR_2 = 0.0955
Largest diff. peak and hole ($e \cdot Å^{-3}$)	0.905 and -1.099

[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. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $BaTi(IO_3)_6 \cdot 0.5H_2O$ U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}	BVS
Ba(1)	0	0	5029(1)	13(1)	2.405
Ba(2)	13333	6667	7032(1)	18(1)	1.879
Ti(1)	6667	3333	5907(2)	11(1)	4.379
Ti(2)	3333	6667	4111(2)	14(1)	4.382
I(1)	9118(1)	4513(1)	7017(1)	13(1)	5.127
I(2)	3095(1)	3883(1)	4819(1)	15(1)	5.119
I(3)	4564(1)	5379(1)	3013(1)	14(1)	5.018
I(4)	6809(1)	5980(1)	5090(1)	15(1)	4.992
O(1)	13333	6667	5941(13)	43(7)	0.395[a], 2.05[b]
O(2)	10603(12)	6178(12)	6916(5)	18(3)	2.012
O(3)	2476(15)	5044(14)	4610(5)	24(3)	2.289
O(4)	1556(13)	2772(13)	5222(6)	21(3)	1.951
O(5)	4179(15)	4804(14)	5392(6)	25(3)	1.882
O(6)	4055(13)	5714(13)	3710(5)	19(3)	2.262
O(7)	8006(14)	5049(13)	7327(5)	18(3)	1.900
O(8)	5076(14)	7033(13)	2698(6)	24(3)	1.849
O(9)	8356(14)	4227(15)	6318(5)	23(3)	2.339
O(10)	8421(13)	7152(13)	4765(5)	18(3)	1.965
O(11)	7481(14)	4939(13)	5413(6)	21(3)	2.202
O(12)	6205(13)	5602(13)	3177(6)	21(3)	1.979
O(13)	5972(14)	4934(14)	4490(6)	24(3)	1.898

a. BVS of O without hydrogen coordinates.

b. BVS with H atoms after geometry optimization.

Table S3. Selected bond distances (Å) and angles (deg) for $BaTi(IO_3)_6 \cdot 0.5H_2O$.

Ba(1)-O(4)	2.733(14)	O(8)#8-Ba(1)-O(7)#10	118.9(3)
Ba(1)-O(4)#1	2.733(13)	O(7)#9-Ba(1)-O(7)#10	59.8(4)
Ba(1)-O(4)#2	2.733(13)	O(4)-Ba(1)-O(7)#11	122.1(4)
Ba(1)-O(10)#3	2.837(13)	O(4)#1-Ba(1)-O(7)#11	107.2(4)
Ba(1)-O(10)#4	2.837(13)	O(4)#2-Ba(1)-O(7)#11	65.7(4)
Ba(1)-O(10)#5	2.837(13)	O(10)#3-Ba(1)-O(7)#11	70.5(4)
Ba(1)-O(8)#6	2.994(14)	O(10)#4-Ba(1)-O(7)#11	54.9(4)
Ba(1)-O(8)#7	2.994(15)	O(10)#5-Ba(1)-O(7)#11	111.2(4)
Ba(1)-O(8)#8	2.994(14)	O(8)#6-Ba(1)-O(7)#11	118.9(3)
Ba(1)-O(7)#9	3.037(12)	O(8)#7-Ba(1)-O(7)#11	119.3(4)
Ba(1)-O(7)#10	3.037(12)	O(8)#8-Ba(1)-O(7)#11	178.6(4)
Ba(1)-O(7)#11	3.038(12)	O(7)#9-Ba(1)-O(7)#11	59.8(4)
Ba(2)-O(1)	2.62(3)	O(7)#10-Ba(1)-O(7)#11	59.8(4)
Ba(2)-O(2)	2.836(13)	O(1)-Ba(2)-O(2)	84.4(3)
Ba(2)-O(2)#12	2.836(13)	O(1)-Ba(2)-O(2)#12	84.4(3)
Ba(2)-O(2)#13	2.836(13)	O(2)-Ba(2)-O(2)#12	119.05(9)
Ba(2)-O(13)#14	2.969(13)	O(1)-Ba(2)-O(2)#13	84.4(3)
Ba(2)-O(13)#15	2.969(13)	O(2)-Ba(2)-O(2)#13	119.05(9)
Ba(2)-O(13)#16	2.969(13)	O(2)#12-Ba(2)-O(2)#13	119.05(9)
Ba(2)-O(12)#14	3.097(13)	O(1)-Ba(2)-O(13)#14	129.8(3)
Ba(2)-O(12)#15	3.097(13)	O(2)-Ba(2)-O(13)#14	145.2(4)
Ba(2)-O(12)#16	3.097(13)	O(2)#12-Ba(2)-O(13)#14	66.2(4)
Ti(1)-O(9)	1.912(14)	O(2)#13-Ba(2)-O(13)#14	76.7(4)
Ti(1)-O(9)#17	1.912(13)	O(1)-Ba(2)-O(13)#15	129.8(3)
Ti(1)-O(9)#3	1.912(13)	O(2)-Ba(2)-O(13)#15	76.7(4)
Ti(1)-O(11)#17	1.957(13)	O(2)#12-Ba(2)-O(13)#15	145.2(4)
Ti(1)-O(11)#3	1.957(13)	O(2)#13-Ba(2)-O(13)#15	66.2(4)
Ti(1)-O(11)	1.957(13)	O(13)#14-Ba(2)-O(13)#15	83.5(4)
Ti(2)-O(6)	1.891(12)	O(1)-Ba(2)-O(13)#16	129.8(3)
Ti(2)-O(6)#5	1.891(12)	O(2)-Ba(2)-O(13)#16	66.2(4)
Ti(2)-O(6)#18	1.891(12)	O(2)#12-Ba(2)-O(13)#16	76.7(4)
Ti(2)-O(3)#5	1.977(13)	O(2)#13-Ba(2)-O(13)#16	145.2(4)
Ti(2)-O(3)#18	1.977(13)	O(13)#14-Ba(2)-O(13)#16	83.5(4)
Ti(2)-O(3)	1.977(13)	O(13)#15-Ba(2)-O(13)#16	83.5(4)
I(1)-O(2)	1.788(12)	O(1)-Ba(2)-O(12)#14	66.2(3)
I(1)-O(7)	1.792(12)	O(2)-Ba(2)-O(12)#14	150.5(4)
I(1)-O(9)	1.835(12)	O(2)#12-Ba(2)-O(12)#14	60.9(4)
I(2)-O(5)	1.782(14)	O(2)#13-Ba(2)-O(12)#14	59.8(4)
I(2)-O(4)	1.818(12)	O(13)#14-Ba(2)-O(12)#14	64.0(4)
I(2)-O(3)	1.822(14)	O(13)#15-Ba(2)-O(12)#14	121.4(4)
I(3)-O(12)	1.771(13)	O(13)#16-Ba(2)-O(12)#14	133.8(4)
I(3)-O(8)	1.807(13)	O(1)-Ba(2)-O(12)#15	66.2(3)
I(3)-O(6)	1.866(12)	O(2)-Ba(2)-O(12)#15	59.8(4)

I(4)-O(10)	1.794(12)	O(2)#12-Ba(2)-O(12)#15	150.5(4)
I(4)-O(13)	1.797(12)	O(2)#13-Ba(2)-O(12)#15	60.9(4)
I(4)-O(11)	1.844(13)	O(13)#14-Ba(2)-O(12)#15	133.8(4)
O(1)-H(1)	0.8927	O(13)#15-Ba(2)-O(12)#15	64.0(4)
O(1)-H(1)#13	0.893(18)	O(13)#16-Ba(2)-O(12)#15	121.4(4)
O(1)-H(1)#12	0.893(18)	O(12)#14-Ba(2)-O(12)#15	104.8(3)
O(4)-Ba(1)-O(4)#1	117.19(17)	O(1)-Ba(2)-O(12)#16	66.2(3)
O(4)-Ba(1)-O(4)#2	117.19(17)	O(2)-Ba(2)-O(12)#16	60.9(4)
O(4)#1-Ba(1)-O(4)#2	117.19(17)	O(2)#12-Ba(2)-O(12)#16	59.8(4)
O(4)-Ba(1)-O(10)#3	63.3(4)	O(2)#13-Ba(2)-O(12)#16	150.5(4)
O(4)#1-Ba(1)-O(10)#3	176.8(4)	O(13)#14-Ba(2)-O(12)#16	121.4(4)
O(4)#2-Ba(1)-O(10)#3	64.2(4)	O(13)#15-Ba(2)-O(12)#16	133.8(4)
O(4)-Ba(1)-O(10)#4	176.8(4)	O(13)#16-Ba(2)-O(12)#16	64.0(4)
O(4)#1-Ba(1)-O(10)#4	64.2(4)	O(12)#14-Ba(2)-O(12)#16	104.8(3)
O(4)#2-Ba(1)-O(10)#4	63.3(4)	O(12)#15-Ba(2)-O(12)#16	104.8(3)
O(10)#3-Ba(1)-O(10)#4	115.18(19)	O(9)-Ti(1)-O(9)#17	95.8(5)
O(4)-Ba(1)-O(10)#5	64.2(4)	O(9)-Ti(1)-O(9)#3	95.8(5)
O(4)#1-Ba(1)-O(10)#5	63.3(4)	O(9)#17-Ti(1)-O(9)#3	95.8(5)
O(4)#2-Ba(1)-O(10)#5	176.8(4)	O(9)-Ti(1)-O(11)#17	89.8(6)
O(10)#3-Ba(1)-O(10)#5	115.17(19)	O(9)#17-Ti(1)-O(11)#17	87.0(6)
O(10)#4-Ba(1)-O(10)#5	115.17(19)	O(9)#3-Ti(1)-O(11)#17	173.4(6)
O(4)-Ba(1)-O(8)#6	72.9(4)	O(9)-Ti(1)-O(11)#3	173.4(6)
O(4)#1-Ba(1)-O(8)#6	115.6(4)	O(9)#17-Ti(1)-O(11)#3	89.8(6)
O(4)#2-Ba(1)-O(8)#6	56.8(4)	O(9)#3-Ti(1)-O(11)#3	87.0(6)
O(10)#3-Ba(1)-O(8)#6	67.6(4)	O(11)#17-Ti(1)-O(11)#3	87.1(6)
O(10)#4-Ba(1)-O(8)#6	109.3(4)	O(9)-Ti(1)-O(11)	87.0(6)
O(10)#5-Ba(1)-O(8)#6	126.1(3)	O(9)#17-Ti(1)-O(11)	173.4(6)
O(4)-Ba(1)-O(8)#7	115.6(4)	O(9)#3-Ti(1)-O(11)	89.8(6)
O(4)#1-Ba(1)-O(8)#7	56.8(4)	O(11)#17-Ti(1)-O(11)	87.1(6)
O(4)#2-Ba(1)-O(8)#7	72.9(4)	O(11)#3-Ti(1)-O(11)	87.1(6)
O(10)#3-Ba(1)-O(8)#7	126.1(3)	O(6)-Ti(2)-O(6)#5	96.4(5)
O(10)#4-Ba(1)-O(8)#7	67.6(4)	O(6)-Ti(2)-O(6)#18	96.4(5)
O(10)#5-Ba(1)-O(8)#7	109.3(4)	O(6)#5-Ti(2)-O(6)#18	96.4(5)
O(8)#6-Ba(1)-O(8)#7	62.0(4)	O(6)-Ti(2)-O(3)#5	173.0(6)
O(4)-Ba(1)-O(8)#8	56.8(4)	O(6)#5-Ti(2)-O(3)#5	86.5(6)
O(4)#1-Ba(1)-O(8)#8	72.9(4)	O(6)#18-Ti(2)-O(3)#5	89.6(6)
O(4)#2-Ba(1)-O(8)#8	115.6(4)	O(6)-Ti(2)-O(3)#18	89.6(6)
O(10)#3-Ba(1)-O(8)#8	109.3(4)	O(6)#5-Ti(2)-O(3)#18	173.0(6)
O(10)#4-Ba(1)-O(8)#8	126.1(3)	O(6)#18-Ti(2)-O(3)#18	86.5(6)
O(10)#5-Ba(1)-O(8)#8	67.6(4)	O(3)#5-Ti(2)-O(3)#18	87.1(6)
O(8)#6-Ba(1)-O(8)#8	62.0(4)	O(6)-Ti(2)-O(3)	86.5(6)
O(8)#7-Ba(1)-O(8)#8	62.0(4)	O(6)#5-Ti(2)-O(3)	89.6(6)
O(4)-Ba(1)-O(7)#9	107.2(4)	O(6)#18-Ti(2)-O(3)	173.0(6)
O(4)#1-Ba(1)-O(7)#9	65.7(4)	O(3)#5-Ti(2)-O(3)	87.1(6)

O(4)#2-Ba(1)-O(7)#9	122.1(4)	O(3)#18-Ti(2)-O(3)	87.1(6)
(10)#3-Ba(1)-O(7)#9	111.2(4)	O(2)-I(1)-O(7)	98.4(6)
O(10)#4-Ba(1)-O(7)#9	70.5(4)	O(2)-I(1)-O(9)	99.6(6)
O(10)#5-Ba(1)-O(7)#9	54.9(4)	O(7)-I(1)-O(9)	95.7(6)
O(8)#6-Ba(1)-O(7)#9	178.6(4)	O(5)-I(2)-O(4)	97.1(7)
O(8)#7-Ba(1)-O(7)#9	118.9(3)	O(5)-I(2)-O(3)	101.1(6)
O(8)#8-Ba(1)-O(7)#9	119.3(4)	O(4)-I(2)-O(3)	93.8(6)
O(4)-Ba(1)-O(7)#10	65.7(4)	O(12)-I(3)-O(8)	100.0(6)
O(4)#1-Ba(1)-O(7)#10	122.1(4)	O(12)-I(3)-O(6)	99.8(6)
O(4)#2-Ba(1)-O(7)#10	107.2(4)	O(8)-I(3)-O(6)	98.2(6)
O(10)#3-Ba(1)-O(7)#10	54.9(4)	O(10)-I(4)-O(11)	93.8(6)
O(10)#4-Ba(1)-O(7)#10	111.2(4)	O(13)-I(4)-O(11)	99.8(6)
O(10)#5-Ba(1)-O(7)#10	70.5(4)	H(1)-O(1)-H(1)#13	107.9
O(8)#6-Ba(1)-O(7)#10	119.3(4)	H(1)-O(1)-H(1)#12	107.9
O(8)#7-Ba(1)-O(7)#10	178.6(4)	H(1)#13-O(1)-H(1)#12	107.9

Symmetry transformations used to generate equivalent atoms:

#1 -y,x-y,z #2 -x+y,-x,z #3 -y+1,x-y,z #4 x-1,y-1,z

#5 -x+y,-x+1,z #6 x-1/3,y-2/3,z+1/3 #7 -x+y-1/3,-x+1/3,z+1/3

#8 -y+2/3,x-y+1/3,z+1/3 #9 -y+1/3,x-y-1/3,z-1/3

#10 x-2/3,y-1/3,z-1/3 #11 -x+y+1/3,-x+2/3,z-1/3

#12 -x+y+2,-x+2,z #13 -y+2,x-y,z #14 -x+y+5/3,-x+4/3,z+1/3

#15 -y+5/3,x-y+1/3,z+1/3 #16 x+2/3,y+1/3,z+1/3

#17 -x+y+1,-x+1,z #18 -y+1,x-y+1,z #19 x+1/3,y+2/3,z-1/3
#20 x+1,y+1,z

Table S4a. Selected Bond Lengths, Experimental Bond Valences, Theoretical Bond Valences, Bond Valence Sums, and BSI and GII Indices for $BaTi(IO_3)_6 \cdot 0.5H_2O$. [a]

		Ba1	Ba2	Ti1	Ti2	I1	I2	I3	I4	H	$V_i = \sum_i S_{ij}$ $z_i = \sum_i S_{ij}$
O1	R_{ij} (Å)		2.628							0.95×2	
	S_{ij} (vu)		0.396							0.832	2.05
	S_{ij} (vu)										
O2	R_{ij} (Å)		2.838×3			1.788					
	S_{ij} (vu)		0.224			1.788					2.01
	S_{ij} (vu)		0.208			1.792					2.00
O3	R_{ij} (Å)				1.978×3		1.819				
	S_{ij} (vu)				0.64543		1.644				2.29
	S_{ij} (vu)				0.7447		1.255				2.00
O4	R_{ij} (Å)	2.732×3					1.817				
	S_{ij} (vu)	0.2982					1.653				1.95
	S_{ij} (vu)	0.255					1.744				2.00
O5	R_{ij} (Å)						1.781				
	S_{ij} (vu)						1.822				1.82
	S_{ij} (vu)						2				2.00
O6	R_{ij} (Å)				1.89×3			1.867			
	S_{ij} (vu)				0.816521			1.444			2.26
	S_{ij} (vu)				0.5886			1.411			2.00
O7	R_{ij} (Å)	3.036×3				1.792					
	S_{ij} (vu)	0.1311				1.769					1.90
	S_{ij} (vu)	0.125				1.875					2.00
O8	R_{ij} (Å)	2.996×3						1.805			
	S_{ij} (vu)	0.1469						1.708			1.85
	S_{ij} (vu)	0.161						1.839			2.00
O9	R_{ij} (Å)			1.913×3		1.836					
	S_{ij} (vu)			0.767		1.570					2.34
	S_{ij} (vu)			0.667		1.333					2.00
O10	R_{ij} (Å)	2.836×3							1.798		
	S_{ij} (vu)	0.224							1.740		1.97
	S_{ij} (vu)	0.125							1.875		2.00
O11	R_{ij} (Å)			1.952×3					1.850		
	S_{ij} (vu)			0.692					1.512		2.20
	S_{ij} (vu)			0.667					1.333		2.00
O12	R_{ij} (Å)		3.094×3					1.772			
	S_{ij} (vu)		0.1121					1.867			1.98
	S_{ij} (vu)		0.25					1.750			2.00
O13	R_{ij} (Å)		2.968×3						1.798		
	S_{ij} (vu)		0.1586						1.740		1.90
	S_{ij} (vu)		0.208						1.797		2.00
$V_j = \sum_j S_{ij}$		2.41	1.88	4.38	4.38	5.13	5.12	5.02	4.99		BSI = 0.12
$z_j = \sum_j S_{ij}$		2.00	2.00	4.00	4.00	5.00	5.00	5.00	5.00		GII = 0.20

Table S4b. Selected Bond Lengths, Experimental Bond Valences, Theoretical Bond Valences, Bond Valence Sums, and BSI and GII Indices for α-$BaTi(IO_3)_6$. [a]

		Ba	Ti	I	$V_i = \sum_i S_{ij}$ $z_i = \sum_i S_{ij}$
O1	R_{ij} (Å)		1.95×6	1.86	
	S_{ij} (vu)		0.694	1.471	2.17
	S_{ij} (vu)		0.667	1.333	2.00
O2	R_{ij} (Å)	2.803×6		1.779	
	S_{ij} (vu)	0.247		1.832	2.08
	S_{ij} (vu)	0.167		1.833	2.00
O3	R_{ij} (Å)	2.955×6		1.805	
	S_{ij} (vu)	0.164		1.708	1.87
	S_{ij} (vu)	0.167		1.833	2.00
	$V_j = \sum_j S_{ij}$	2.46	4.17	5.01	BSI = 0.06
	$z_j = \sum_j S_{ij}$	2.00	4.00	5.00	GII = 0.22

Table S4c. Selected Bond Lengths, Experimental Bond Valences, Theoretical Bond Valences, Bond Valence Sums, and BSI and GII Indices for β-$BaTi(IO_3)_6$. [a]

		Ba	Ti	I	$V_i = \sum_i S_{ij}$ $z_i = \sum_i S_{ij}$
O1	R_{ij} (Å)	3.031×6		1.809	
	S_{ij} (vu)	0.133		1.689	1.82
	S_{ij} (vu)	0.089		1.912	2.00
O2	R_{ij} (Å)	2.805×6		1.78	
	S_{ij} (vu)	0.245		1.827	2.07
	S_{ij} (vu)	0.245		1.755	2.00
O3	R_{ij} (Å)		1.934×6	1.86	
	S_{ij} (vu)		0.725	1.472	2.20
	S_{ij} (vu)		0.667	1.333	2.00
	$V_j = \sum_j S_{ij}$	2.27	4.36	4.99	BSI = 0.07
	$z_j = \sum_j S_{ij}$	2.00	4.00	5.00	GII = 0.21

[a] R_{ij}, bond length of the bond ij; $S_{ij} = \exp[(R_0 - R_{ij})/B]$, experimental bond valence, in valence units (vu), of bond ij, where R_0 is a constant dependent on i and j bonded elements, and B = 0.37 [R_0(Ba−O) = 2.285 Å, R_0(Ti−O) = 1.815 Å, R_0(I−O)= 2.003 Å]; s_{ij}, theoretical bond valence, in valence units (vu), of bond ij, calculated by solving the network equations based on the methods described by Brown; V_i, V_j, experimental valences of anions i and cations j; z_i, z_j, charge or formal valence of anions i and cations j; BSI = $[<(S_{ij} - s_{ij})^2>]^{1/2}$, bond strain index; GII = $[<(V_{i,j} - z_{i,j})^2>]^{1/2}$, global instability index.

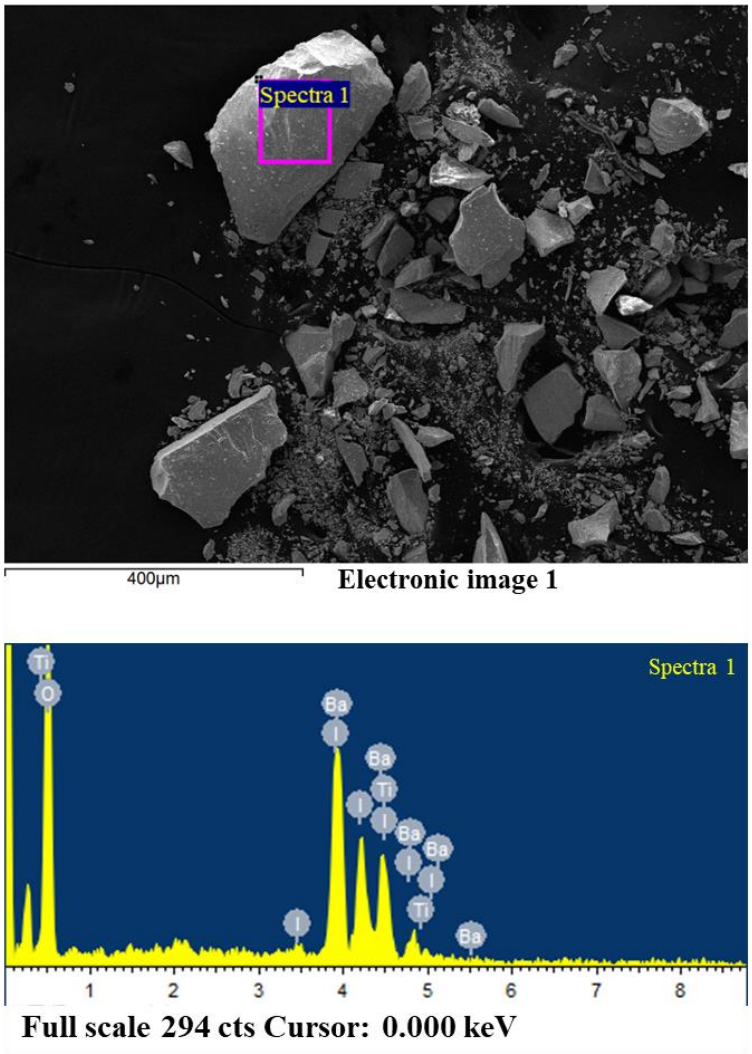

Figure S1. The EDS analysis of $BaTi(IO_3)_6 \cdot 0.5H_2O$.

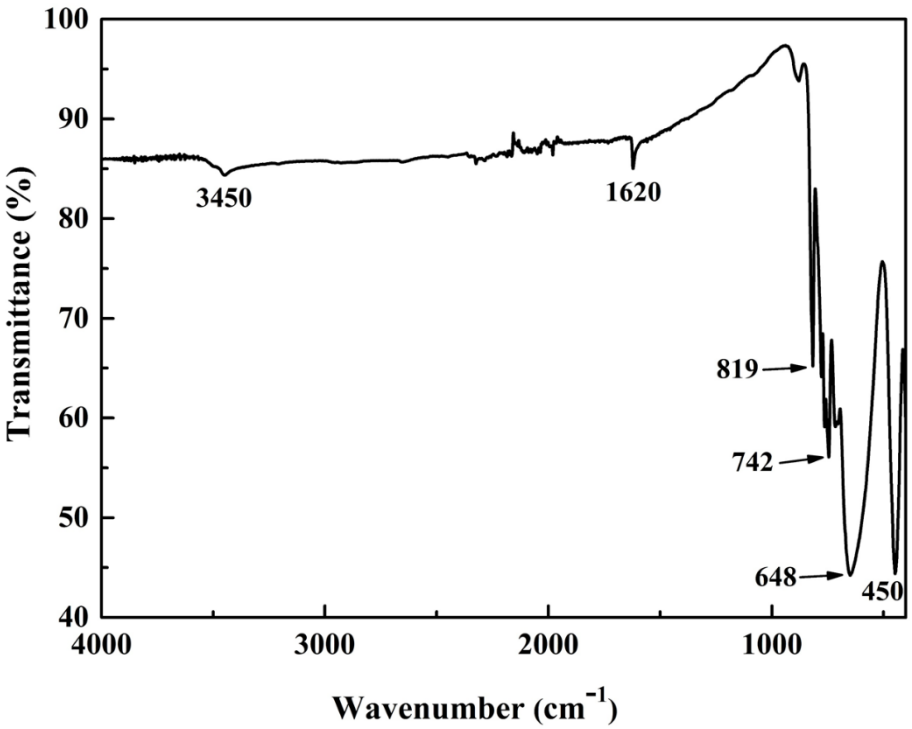

Figure S2. IR spectrum for $BaTi(IO_3)_6 \cdot 0.5H_2O$.

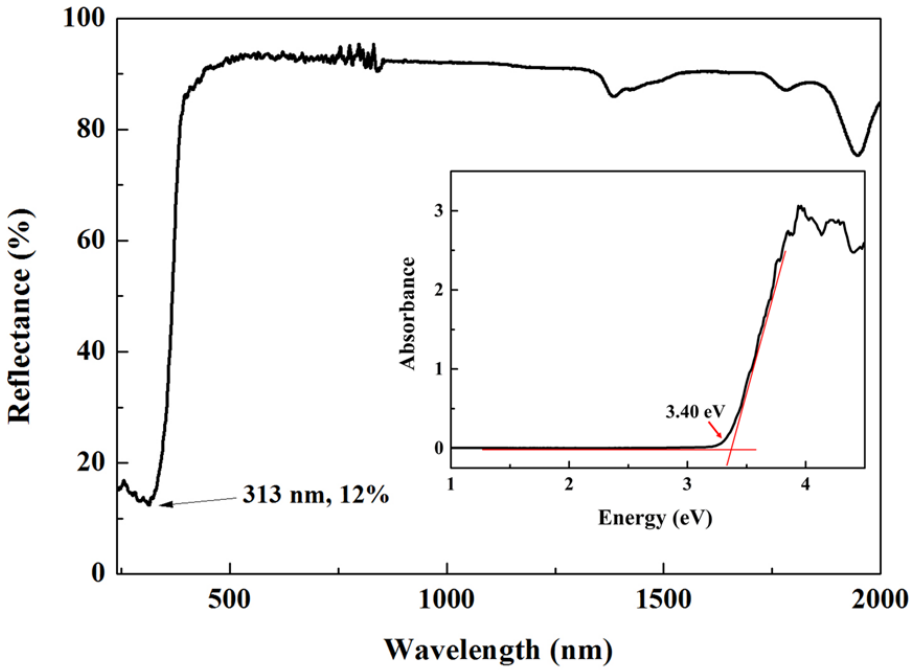

Figure S3. The UV-Vis-NIR diffuse reflectance spectrum for $BaTi(IO_3)_6 \cdot 0.5H_2O$.

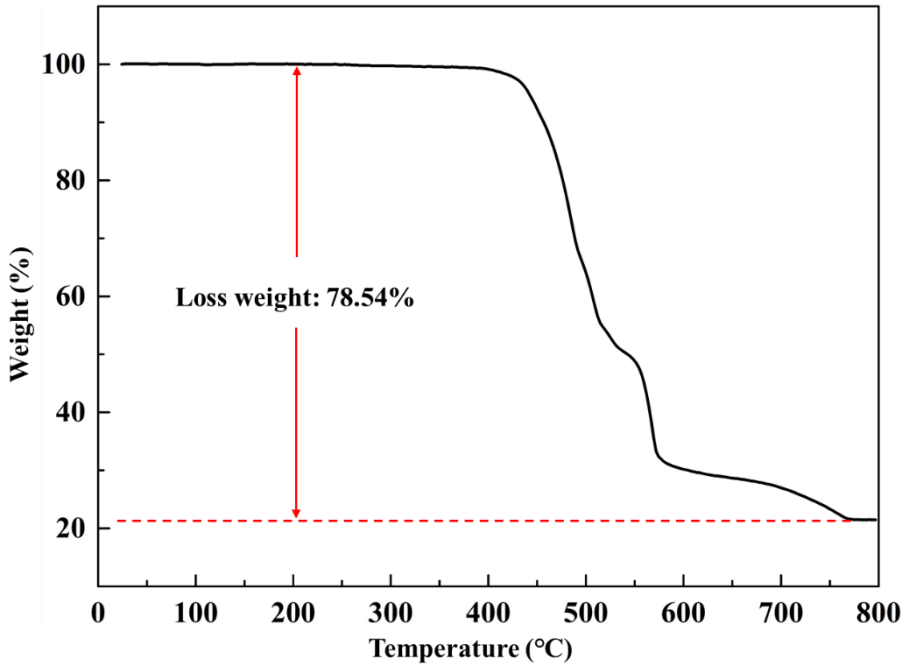

Figure S4. Thermogravimetric analysis diagram for $BaTi(IO_3)_6 \cdot 0.5H_2O$.

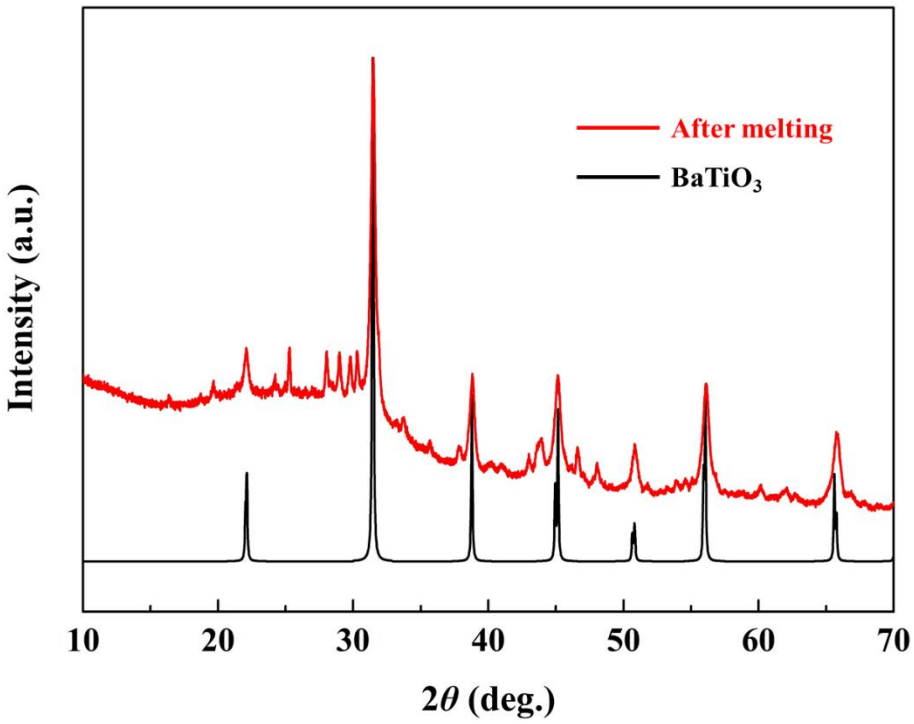

Figure S5. The powder XRD patterns of the $BaTi(IO_3)_6 \cdot 0.5H_2O$ residual after TGA.

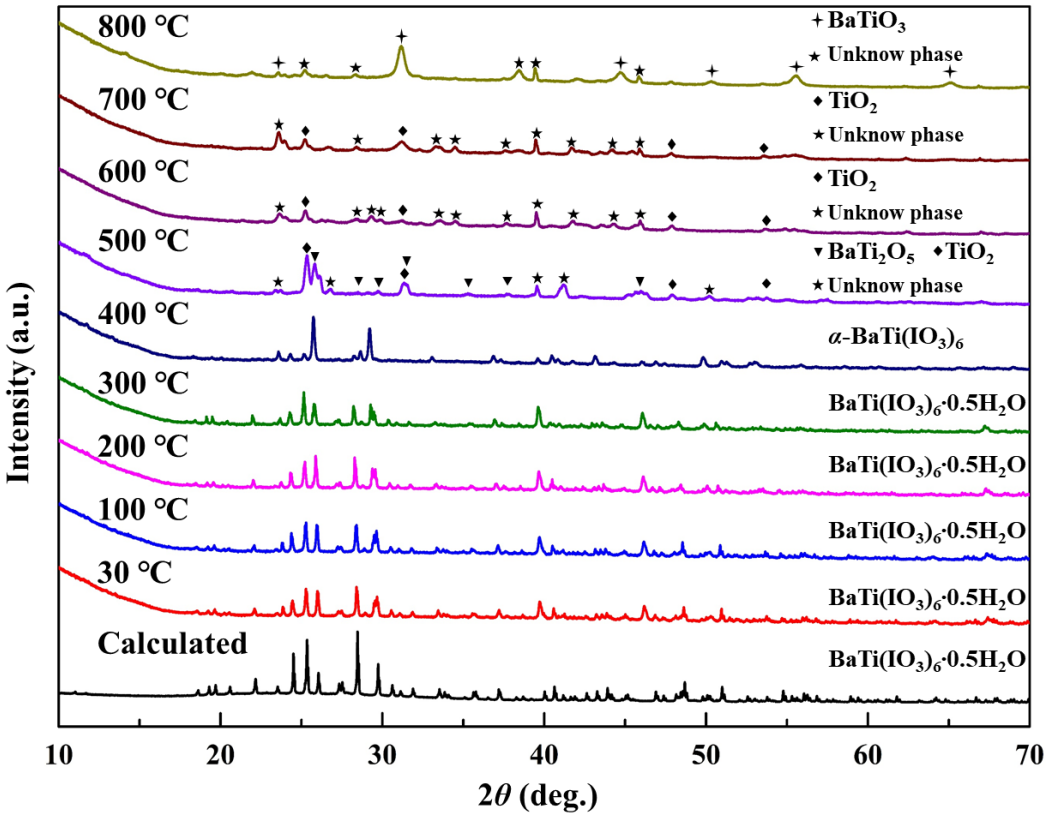

Figure S6. The variable-temperature powder XRD patterns of the $BaTi(IO_3)_6 \cdot 0.5H_2O$.