Electronic Supplementary Material (ESI) for RSC Advances.

β-$BaGa[B_4O_8(OH)](H_2O)$ and $Ba_4Ga[B_{10}O_{18}(OH)_5](H_2O)$: New Barium Galloborates Featuring Unusual $[B_4O_8(OH)]^{2-}$ and $[B_{10}O_{18}(OH)_5]^{11-}$ Clusters

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Supporting Information

Table S1. Important bond lengths (Å) for *β*–$BaGa[B_4O_8(OH)](H_2O)$ and $Ba_4Ga[B_{10}O_{18}(OH)_5](H_2O)$

Table S2. Hydrogen bond lengths (Å) and bond angles(°) of *β*–$BaGa[B_4O_8(OH)](H_2O)$ and $Ba_4Ga[B_{10}O_{18}(OH)_5](H_2O)$.

Table S3. The direction and magnitude of the dipole moments in the GaO_4, BO_3 and BO_4 polyhedra, and net dipole moment in the unit cell of $Ba_4Ga[B_{10}O_{18}(OH)_5](H_2O)$ (D= Debye, Ba^{2+} ions and water molecules were not considered).

Table S4. State energies (electronvolts) of the lowest conduction band (L-CB) and the highest valence band (H–VB) of *β*–$BaGa[B_4O_8(OH)](H_2O)$ and $Ba_4Ga[B_{10}O_{18}(OH)_5](H_2O)$.

Figure S1. Experimental and simulated powder X-ray diffraction patterns of *β*–$BaGa[B_4O_8(OH)](H_2O)$ and $Ba_4Ga[B_{10}O_{18}(OH)_5](H_2O)$. X-ray diffraction patterns of the residues of two compounds which were obtained after thermal annealing (at 700 °C for 5 h).

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Figure S5. UV-vis-NIR diffuse reflectance absorption spectra of *β*–$BaGa[B_4O_8(OH)](H_2O)$ and $Ba_4Ga[B_{10}O_{18}(OH)_5](H_2O)$.

Figure S6. IR spectra of *β*–$BaGa[B_4O_8(OH)](H_2O)$ and $Ba_4Ga[B_{10}O_{18}(OH)_5](H_2O)$.

Figure S7. Thermogravimetric analyses of *β*–$BaGa[B_4O_8(OH)](H_2O)$ and $Ba_4Ga[B_{10}O_{18}(OH)_5](H_2O)$ and *α*–$BaGa[B_4O_8(OH)](H_2O)$.

Figure S8. Ferroelectric hysteresis loop of $Ba_4Ga[B_{10}O_{18}(OH)_5](H_2O)$

Table S1. Important bond lengths (Å) for β-$BaGa[B_4O_8(OH)](H_2O)$ (**1**) and $Ba_4Ga[B_{10}O_{18}(OH)_5](H_2O)$ (**2**)[a]

	β-$BaGa[B_4O_8(OH)](H_2O)$ (**1**)		
Ba(1)-O(1W)	2.699(6)	B(2)-O(8)	1.453(9)
Ba(1)-O(1)#1	2.766(5)	B(2)-O(4)	1.468(9)
Ba(1)-O(7)	2.767(4)	B(2)-O(3)	1.469(9)
Ba(1)-O(5)#2	2.809(4)	B(2)-O(5)	1.483(8)
Ba(1)-O(4)	2.833(4)	B(4)-O(9)	1.346(9)
Ba(1)-O(9)#3	2.912(4)	B(4)-O(5)	1.356(9)
Ba(1)-O(8)#2	2.920(4)	B(4)-O(6)	1.396(8)
Ba(1)-O(9)#4	2.931(5)	B(3)-O(4)	1.347(8)
Ba(1)-O(6)#3	2.965(4)	B(3)-O(8)	1.364(8)
Ba(1)-O(3)#2	3.063(5)	B(3)-O(6)	1.411(8)
Ga(1)-O(7)#5	1.855(4)	B(1)-O(2)	1.339(9)
Ga(1)-O(9)#3	1.865(4)	B(1)-O(1)	1.375(9)
Ga(1)-O(8)	1.882(4)	B(1)-O(3)	1.376(8)
Ga(1)-O(2)	1.932(5)		
Ga(1)-O(8)#6	2.055(5)		
	$Ba_4Ga[B_{10}O_{18}(OH)_5](H_2O)$ (**2**)		
Ba(1)-O(23)#1	2.732(4)	Ga(1)–O(1)	1.846(4)
Ba(1)-O(9)	2.772(4)	Ga(1)–O(19)#10	1.869(4)
Ba(1)-O(2)#2	2.785(3)	B(1)–O(1)	1.363(7)
Ba(1)-O(20)#1	2.812(3)	B(1)–O(3)	1.372(7)
Ba(1)-O(3)	2.922(4)	B(1)–O(2)	1.375(7)
Ba(1)-O(6)#3	2.929(4)	B(2)–O(4)	1.438(7)
Ba(1)-O(11)	2.957(4)	B(2)–O(8)	1.455(7)
Ba(1)-O(7)	2.977(4)	B(2)–O(5)	1.457(7)
Ba(1)-O(17)#1	3.000(3)	B(2)–O(2)	1.554(7)
Ba(1)-O(5)#2	3.050(4)	B(3)–O(7)	1.444(7)
Ba(2)-O(7)#4	2.722(3)	B(3)–O(4)	1.460(7)
Ba(2)-O(5)#3	2.827(4)	B(3)–O(6)	1.470(7)
Ba(2)-O(11)#5	2.834(4)	B(3)–O(3)	1.525(7)
Ba(2)-O(1W)	2.879(4)	B(4)–O(8)	1.455(7)
Ba(2)-O(10)#4	2.879(4)	B(4)–O(9)	1.485(7)
Ba(2)-O(2)	2.881(4)	B(4)–O(7)	1.489(6)
Ba(2)-O(9)	2.893(4)	B(4)–O(10)	1.498(6)
Ba(2)-O(14)	3.117(4)	B(5)–O(11)	1.458(7)
Ba(2)-O(8)	3.180(4)	B(5)–O(12)	1.458(7)
Ba(3)-O(18)	2.746(4)	B(5)–O(9)	1.468(7)
Ba(3)-O(22)#6	2.762(4)	B(5)–O(14)	1.521(7)
Ba(3)-O(6)#7	2.784(3)	B(6)–O(10)	1.429(6)
Ba(3)-O(17)	2.814(4)	B(6)–O(12)	1.465(7)
Ba(3)-O(21)#8	2.816(4)	B(6)–O(13)	1.470(7)
Ba(3)-O(20)#6	2.818(4)	B(6)–O(15)	1.523(7)
Ba(3)-O(3)#7	2.824(3)	B(7)–O(16)	1.356(7)
Ba(3)-O(13)	2.841(4)	B(7)–O(15)	1.373(8)
Ba(3)-O(19)#8	2.888(4)	B(7)–O(14)	1.399(7)
Ba(3)-O(15)	2.914(3)	B(8)–O(20)	1.435(7)
Ba(4)-O(8)	2.652(4)	B(8)–O(17)	1.444(7)
Ba(4)-O(13)#5	2.786(4)	B(8)–O(16)	1.489(6)
Ba(4)-O(14)#8	2.866(4)	B(8)–O(18)	1.523(7)
Ba(4)-O(21)#8	2.872(4)	B(9)–O(18)	1.361(7)
Ba(4)-O(1W)	2.890(4)	B(9)–O(19)	1.366(7)
Ba(4)-O(10)	2.903(4)	B(9)–O(21)	1.374(7)
Ba(4)-O(22)#8	2.958(3)	B(10)–O(20)	1.440(7)
Ba(4)-O(16)#8	2.958(4)	B(10)–O(22)	1.455(7)
Ba(4)-O(15)	2.997(4)	B(10)–O(23)	1.465(7)
Ga(1)–O(17)#1	1.806(4)	B(10)–O(21)	1.519(7)
Ga(1)–O(22)#9	1.816(4)		

[a] Symmetry transformations used to generate equivalent atoms:

For **1**: #1 -x+1, -y+1, -z; #2 x+1, y, z; #3 –x, –y+1, –z; #5 x–1/2, y–1/2,z;#6 –x–1/2,–y+1/2,–z.

For **2**: #1 -x+1, -y+1, -z; #2 x-1, y, z; #3 x-1/2, y-1/2, z; #4 x+1/2, y-1/2, z; #5 x+1, y, z; #6 x-1/2, y+1/2, z; #7 x-1/2, -y+3/2, z-1/2; #8 x+1/2, y+1/2, z; #9 x+1/2, -y+1/2, z+1/2; #10 x+1,-y+1,z+1/2.

Table S2. Hydrogen bond lengths (Å) and bond angles(°)

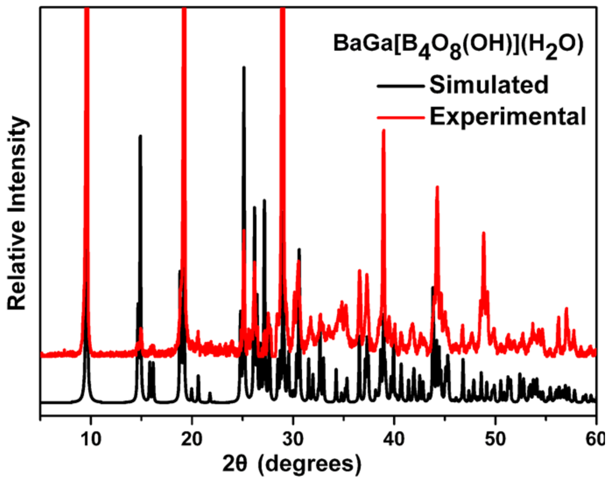
β–$BaGa[B_4O_8(OH)](H_2O)$ (**1**)				
O1-H8A···O2	0.820	1.892	2.700(7)	168.68
O1W-H1WA···O3	0.850	1.888	2.696(8)	158.24
$Ba_4Ga[B_{10}O_{18}(OH)_5](H_2O)$ (**2**)				
O5-H5A···O12	0.82	1.87	2.685(5)	169.1
O11-H11A···O4	0.82	1.91	2.707(5)	165.2
O23-H23A···O1	0.82	2.19	2.996(6)	167.2
O1W-H1WA···O19	0.85	2.15	2.813(5)	134.6
O1W-H1WB···O12	0.85	2.17	2.666(5)	117.3

Table S3 The direction and magnitude of the dipole moments in the GaO_4, BO_3 and BO_4 polyhedra, and net dipole moment in the unit cell of $Ba_4Ga[B_{10}O_{18}(OH)_5](H_2O)$ (**2**) (D= Debye, Ba^{2+} ions and water molecules were not considered).

Species	**Total magnitude**	**x (D)**	**y (D)**	**z (D)**
$B(1)O_3$	1.33	-0.62	±0.72	-0.92
$B(7)O_3$	1.46	-0.47	±1.36	0.26
$B(9)O_3$	0.98	-0.017	±0.96	0.20
$B(2)O_4$	2.10	0.62	±1.64	1.15
$B(3)O_4$	1.56	0.67	±0.37	1.35
$B(4)O_4$	0.84	-0.49	±0.67	-0.082
$B(5)O_4$	1.17	-0.30	±0.33	-1.09
$B(6)O_4$	2.14	-1.12	±1.00	-1.52
$B(8)O_4$	1.98	-1.97	0	0.23
$B(10)O_4$	0.97	-0.53	±0.80	0.072
GaO_4	1.17	0.89	±0.57	0.49
Net dipole moment (a unit cell)	13.44	-13.42	0	0.67

Table S4. State energies (electronvolts) of the lowest conduction band (L-CB) and the highest valence band (H-VB) of *β*–$BaGa[B_4O_8(OH)](H_2O)$ (**1**) and $Ba_4Ga[B_{10}O_{18}(OH)_5](H_2O)$ (**2**)

	k-point	L-CB	H-VB
β–$BaGa[B_4O_8(OH)](H_2O)$ (**1**)	V(0.000 0.000 0.500)	5.43195	-0.01745
	G(0.000 0.000 0.000)	5.17593	-0.02285
	F(0.000 0.500 0.000)	6.23751	-0.08155
	Q(0.000 0.500 0.500)	6.32449	-0.02391
	Z(0.000 0.000 0.500)	5.90506	-0.0028
	G(0.000 0.000 0.000)	5.17593	-0.02285
$Ba_4Ga[B_{10}O_{18}(OH)_5](H_2O)$ (**2**)	Z(0.000 0.000 0.500)	4.39315	-0.00103
	G(0.000 0.000 0.000)	4.29691	-0.00047
	Y(0.000 0.500 0.000)	4.58321	-0.00352
	A(-0.500 0.500 0.000)	4.92749	-0.00735
	B(-0.500 0.000 0.000)	4.96056	-0.1273
	D(-0.500 0.000 0.500)	4.98638	-0.01279
	E(-0.500 0.500 0.500)	4.92245	-0.00741
	C(0.000 0.500 0.500)	4.64867	-0.00506



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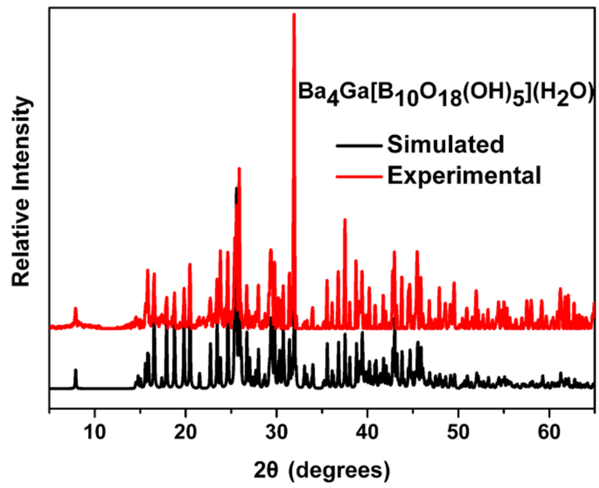

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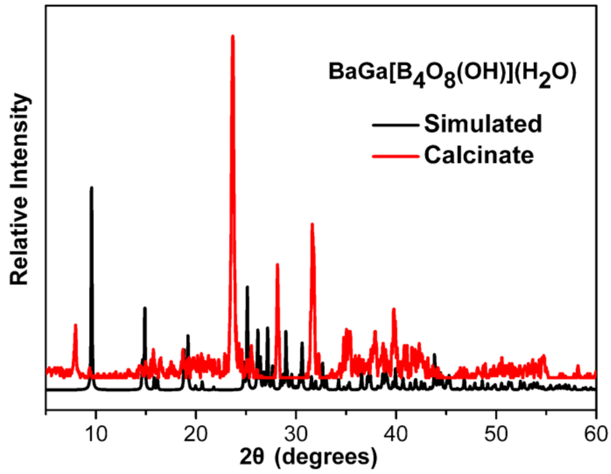

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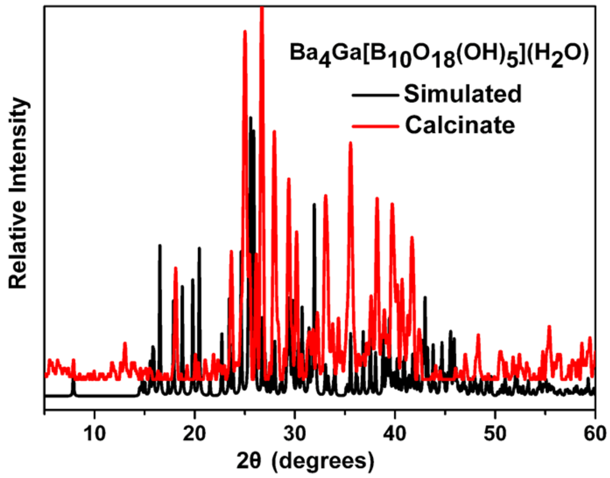


(d)

Figure S1. Experimental and simulated powder X-ray diffraction patterns of *β*–$BaGa[B_4O_8(OH)](H_2O)$ (**1**) (a) and $Ba_4Ga[B_{10}O_{18}(OH)_5](H_2O)$ (**2**) (b). X-ray diffraction patterns of the residues of *β*–$BaGa[B_4O_8(OH)](H_2O)$ (**1**) (c) and $Ba_4Ga[B_{10}O_{18}(OH)_5](H_2O)$ (**2**) (d) which were obtained after thermal annealing (at 700 °C for 5 h).

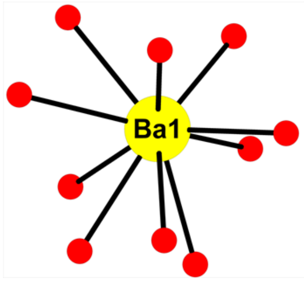


Figure S2 View of the coordination environments around the Ba atoms in *β*–$BaGa[B_4O_8(OH)](H_2O)$ (**1**). Ba and O atoms are drawn as yellow and red circles, respectively.

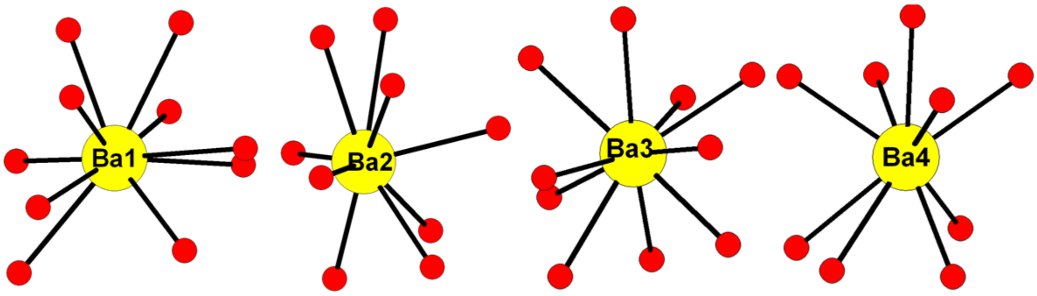


Figure S3. View of the coordination environments around the Ba atoms in $Ba_4Ga[B_{10}O_{18}(OH)_5](H_2O)$ (**2**). Ba and O atoms are drawn as yellow and red circles, respectively.

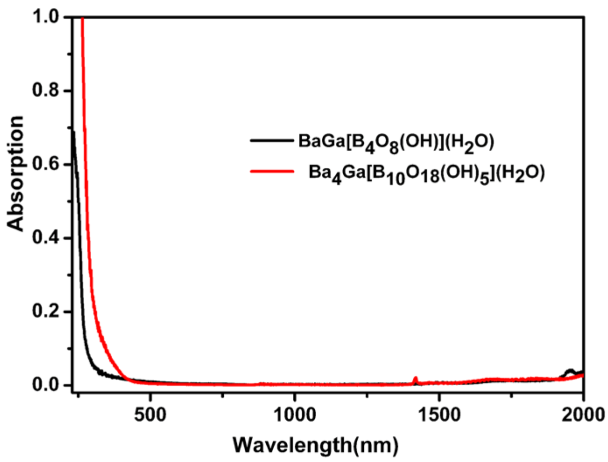
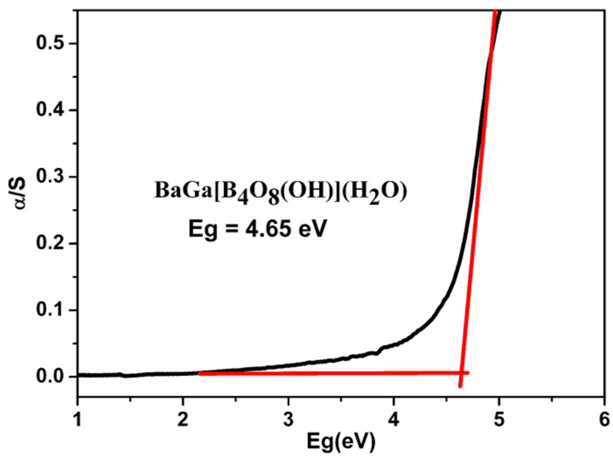


Figure S4. UV-vis-NIR absorption spectra of *β*–$BaGa[B_4O_8(OH)](H_2O)$ (**1**) and $Ba_4Ga[B_{10}O_{18}(OH)_5](H_2O)$ (**2**).



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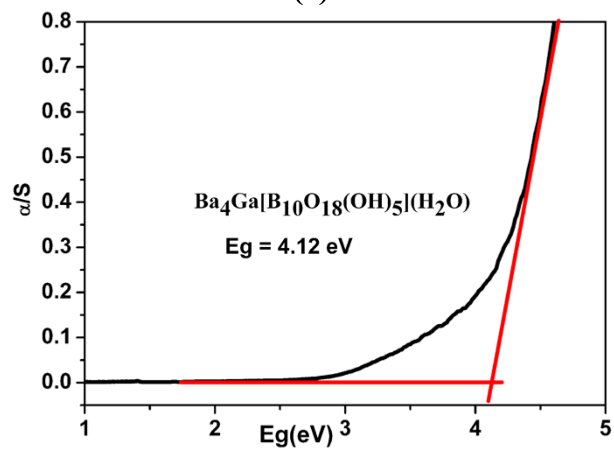
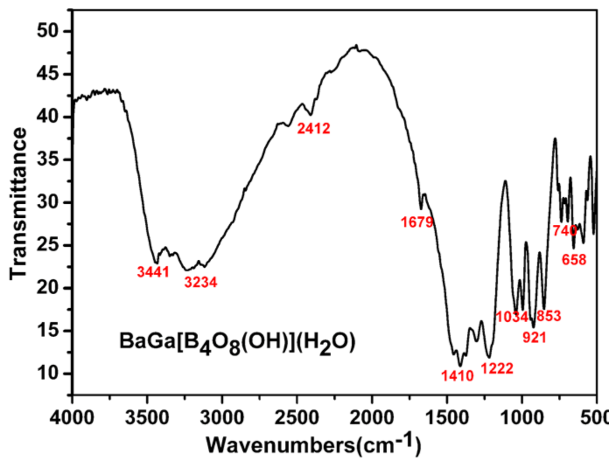
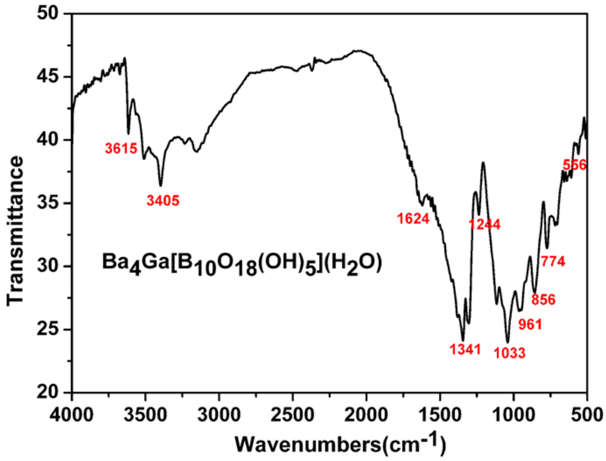


(b)

Figure S5. UV-vis-NIR diffuse reflectance absorption spectra of β–BaGa[B_4O_8(OH)](H_2O) (**1**) and Ba_4Ga[$B_{10}O_{18}(OH)_5$](H_2O) (**2**).

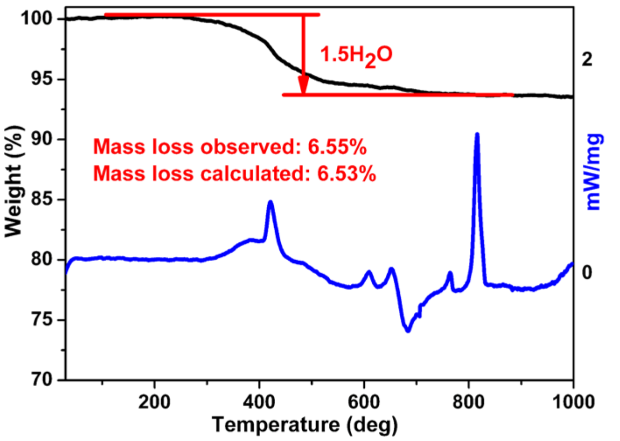


(**a**)



(b)

Figure S6. IR spectra of β–$BaGa[B_4O_8(OH)](H_2O)$ (**1**) and $Ba_4Ga[B_{10}O_{18}(OH)_5](H_2O)$ (**2**).



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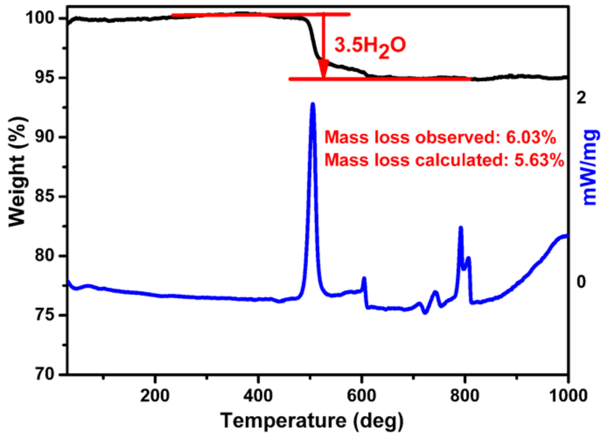

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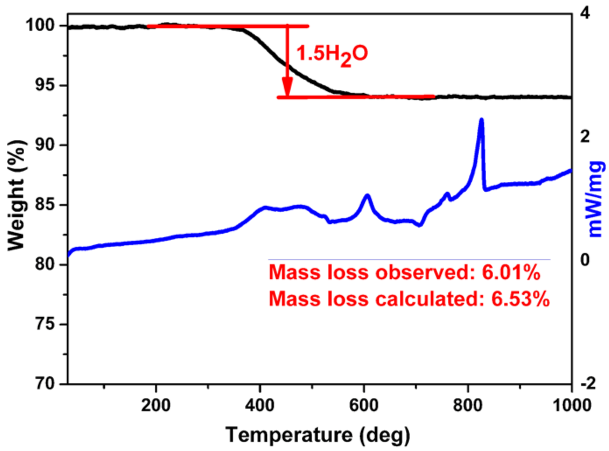

(c)

Figure S7. Thermogravimetric analyses of *β*–BaGa[B_4O_8(OH)](H_2O) (**1**) (a), Ba_4Ga[$B_{10}O_{18}(OH)_5$](H_2O) (**2**) (b) and *α*–BaGa[B_4O_8(OH)](H_2O) (c).

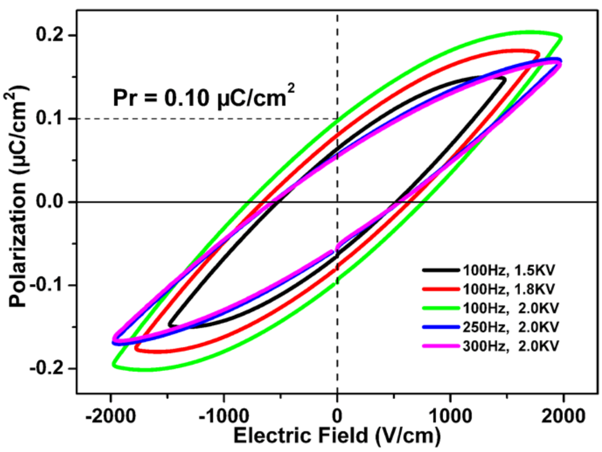

Figure S8. Ferroelectric hysteresis loop of compound Ba_4Ga[$B_{10}O_{18}(OH)_5$](H_2O) (**2**)