

Supporting Information

A new $\text{I}_3\text{O}_9^{3-}$ group constructed by IO_3^- and IO_5^{5-} anion units in $\text{Cs}_3[\text{Ga}_2\text{O}(\text{I}_3\text{O}_9)(\text{IO}_3)_4(\text{HIO}_3)]$

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1. Supplementary Tables.

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Atom	x	y	z	$U_{(\text{eq})}^a$
I1	5103.8(6)	2500	3106.2(6)	6.61(12)
I2	2485.8(5)	3862.0(2)	3689.7(5)	7.51(10)
I3	7418.2(5)	4483.9(2)	3774.8(5)	7.97(11)
I4	8025.8(5)	4518.7(2)	9072.5(4)	6.48(10)
I5	10259.4(6)	2500	6011.2(6)	7.12(12)
Cs1	9061.3(8)	2500	709.8(8)	21.23(15)
Cs2	3356.8(5)	3811.5(2)	976.3(5)	15.38(11)
Ga1	6964.4(8)	3378.3(3)	6322.7(8)	6.04(14)
O1	5234(9)	2500	1118(8)	18.6(14)
O2	2743(6)	3328(2)	2164(6)	17.1(9)
O3	6795(5)	3140(2)	4064(5)	9.7(8)
O4	615(6)	3487(2)	4014(6)	19.1(10)
O5	4312(6)	3572(2)	5558(5)	13.2(9)
O6	5009(7)	4549(3)	2863(7)	24.4(11)
O7	7624(6)	4249(2)	5883(6)	13.8 (9)
O8	8067(8)	5295(2)	4194(7)	22.6(11)
O9	7240(5)	36980(19)	8514(5)	8.1(8)
O10	10365(6)	4342(2)	10311(6)	19.7(10)
O11	7084(7)	4633(2)	10626(6)	20.8(10)
O12	9557(5)	3132(2)	7102(5)	11.1 (8)
O13	12626(8)	2500	7221(9)	15.9(13)
O14	6283(9)	2500	6768(7)	4.6(14)
H13	13800(2)	2500	7300(7)	300(3)

$^a U_{(\text{eq})}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S2. Selected bond lengths (Å) and calculated bond order (e) of Cs₃[Ga₂O(I₃O₉)(IO₃)₄(HIO₃)] (CGIO).

Bond	Bond length	Bond order
I1-O1	1.764(6)	0.40
I1-O2	2.469(4)	0.04
I1-O2 ¹	2.469(4)	0.04
I1-O3	1.867(4)	0.17
I1-O3 ¹	1.867(4)	0.17
I2-O2	1.806(4)	0.27
I2-O4	1.791(4)	0.32
I2-O5	1.833(4)	0.27
I3-O6	1.780(5)	0.35
I3-O7	1.842(4)	0.17
I3-O8	1.786(5)	0.32
I4-O9	1.845(4)	0.17
I4-O10	1.804(5)	0.27
I4-O11	1.781(4)	0.35
I5-O12	1.837(4)	0.27
I5-O12 ¹	1.837(4)	0.27
I5-O13	1.777(6)	0.35
Ga1-O3	1.978(4)	0.52
Ga1-O5	1.997(4)	0.18
Ga1-O7	1.987(4)	0.29
Ga1-O9	1.951(4)	0.61
Ga1-O12	1.979(4)	0.28
Ga1-O14	2.009(3)	0.13

Table S3. Selected bond angles (°) of Cs₃[Ga₂O(I₃O₉)(IO₃)₄(HIO₃)] (**CGIO**).

Angle	(°)
O1-I1-O3	89.27(19)
O1-I1-O2 ¹	89.27(19)
O1-I1-O3	98.3(2)
O1-I1-O3 ¹	98.3(2)
O2 ¹ -I1-O2	90.2(2)
O3-I1-O2	88.02(17)
O3-I1-O2 ¹	172.26(17)
O3 ¹ -I1-O2	172.26(17)
O3 ¹ -I1-O2 ¹	88.02(17)
O3-I1-O3 ¹	92.7(3)
O2-I2-O5	100.0(2)
O4-I2-O2	99.3(2)
O4-I2-O5	98.1(2)
O6-I3-O7	98.6(2)
O6-I3-O8	101.4(3)
O8-I3-O7	98.2(2)
O10-I4-O9	97.7(2)
O11-I4-O10	101.7(2)
O11-I4-O9	97.5(2)
O12 ¹ -I5-O12	93.2(3)
O13-I5-O12 ¹	98.6(2)
O13-I5-O12	98.6(2)

2. Supplementary Figures.

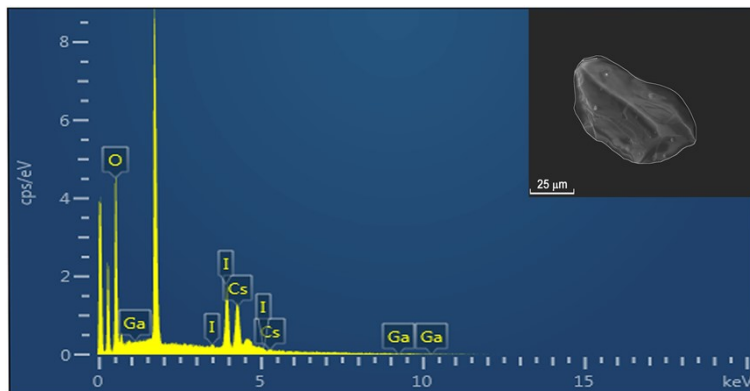


Figure S1. The EDS spectrum of CGIO.

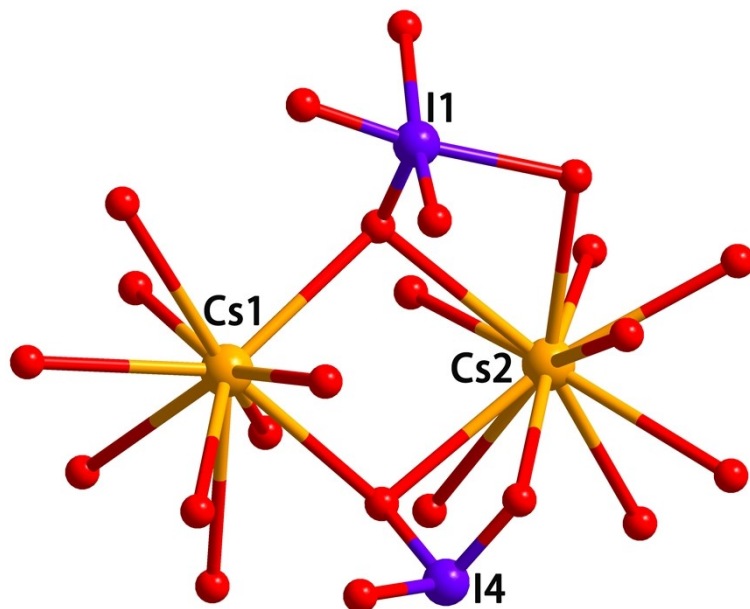


Figure S2. The coordination environments of Cs1 atom and Cs2 atom of crystal **CGIO**.

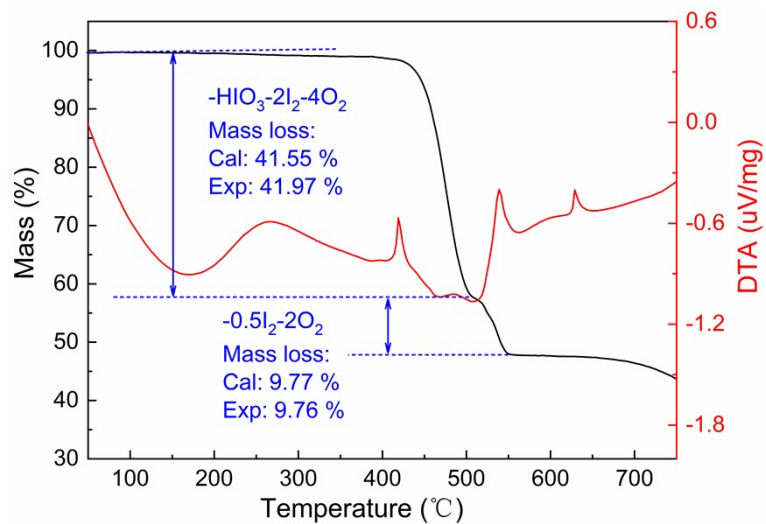


Figure S3. The TG and DTA curves of **CGIO**.

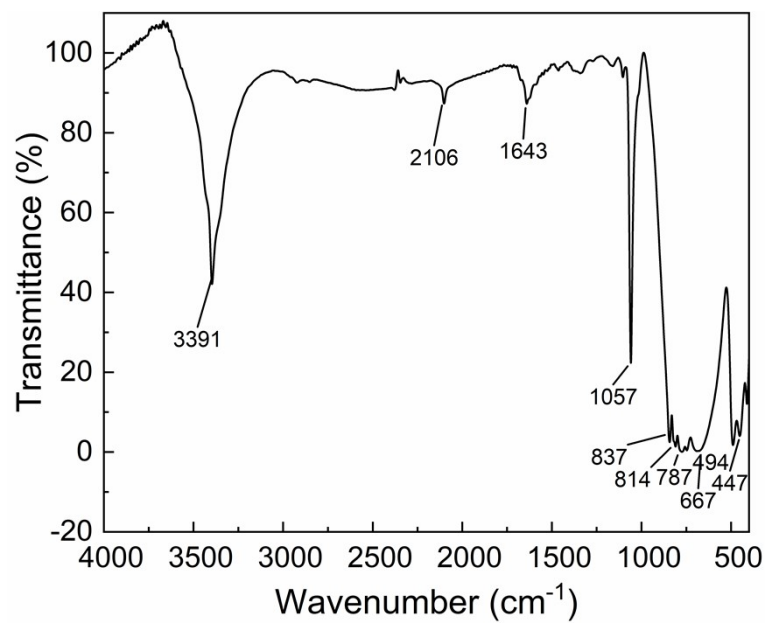


Figure S4. The IR spectrum of CGIO.

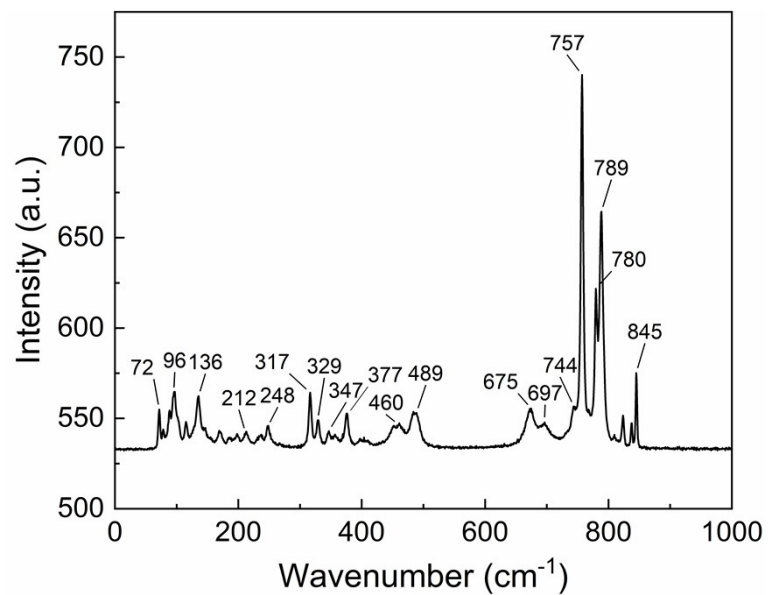


Figure S5. The Raman spectrum of **CGIO**.