Electronic Supplementary Material (ESI) for Dalton Transactions.

A study of composition effects on bandgaps on a series of new alkali metal aluminum/gallium iodates

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Table S1. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for $A_2M(IO_3)_4(H_{0.5}IO_3)_2$ (A=K, Rb; M=Al, Ga).

Atom	Symmetry	*x*	*y*	*z*	$U_{(eq)}$	Occu.
			$K_2Al(IO_3)_4(H_{0.5}IO_3)_2$			
K1	2*i*	8278.8(17)	3406.8(17)	8148.0(18)	20.9(2)	1
Al1	1*f*	5000	10000	5000	8.5(4)	1
I1	2*i*	6929.1(4)	8292.7(4)	1484.0(4)	8.36(7)	1
I2	2*i*	3377.1(4)	6444.7(4)	7119.2(4)	8.64(8)	1
I3	2*i*	8660.8(4)	8122.4(4)	6591.6(4)	9.96(8)	1
O1	2*i*	5486(5)	8078(5)	3253(5)	14.1(7)	1
O2	2*i*	9080(5)	8787(6)	2965(5)	17.7(8)	1
O3	2*i*	6902(6)	5911(5)	725(5)	16.9(8)	1
O4	2*i*	3341(5)	8259(5)	5763(5)	15.4(7)	1
O5	2*i*	949(5)	5893(5)	6888(6)	15.8(7)	1
O6	2*i*	3833(5)	7922(5)	9292(5)	16.7(8)	1
O7	2*i*	6962(5)	9682(5)	6703(5)	13.5(7)	1
O8	2*i*	7118(5)	6072(5)	6343(6)	16.7(8)	1
O9	2*i*	9256(5)	8480(5)	9085(5)	16.0(7)	1
H9	2*i*	9722.74	9530.36	9461	24	0.5
			$Rb_2Al(IO_3)_4(H_{0.5}IO_3)_2$			
Rb1	2*i*	8359.0(8)	8225.7(8)	-1552.5(8)	17.42(14)	1
Al1	1*f*	5000	5000	5000	6.9(4)	1
I1	2*i*	3393.2(4)	7082.8(4)	1476.2(4)	7.89(9)	1
I2	2*i*	3087.9(4)	8490.2(4)	6681.4(4)	7.65(9)	1
I3	2*i*	8641.0(5)	6587.3(5)	3153.3(5)	9.94(10)	1
O1	2*i*	3379(5)	5725(6)	3250(5)	14.3(8)	1
O2	2*i*	1008(5)	6890(6)	990(6)	17.6(9)	1
O3	2*i*	3892(6)	9231(6)	2926(6)	18.0(9)	1
O4	2*i*	4537(5)	6764(5)	6855(5)	12.5(8)	1
O5	2*i*	3100(6)	9178(5)	9028(5)	15.7(9)	1
O6	2*i*	968(5)	6980(6)	6169(6)	19.1(9)	1
O7	2*i*	6978(5)	6682(5)	4686(5)	13.1(8)	1
O8	2*i*	7123(5)	6327(6)	1123(5)	18.2(9)	1
O9	2*i*	9207(6)	9059(5)	3436(6)	16.5(9)	1
H9	2*i*	9695.05	9455.62	4457.83	25	0.5
			$K_2Ga(IO_3)_4(H_{0.5}IO_3)_2$			
K1	2*i*	1709.6(16)	11599.2(16)	1846.9(16)	20.9(2)	1
Al1	1*f*	5000	5000	5000	9.45(16)	1
I1	2*i*	6645.2(4)	8587.9(4)	2876.6(4)	9.60(9)	1
I2	2*i*	6936.9(4)	3276.6(4)	1452.1(4)	9.31(9)	1
I3	2*i*	1305.6(4)	6894.9(4)	3390.0(4)	10.96(9)	1

O1	*2i*	6745(4)	6821(5)	4259(5)	15.5(7)	1
O2	*2i*	9052(4)	9150(5)	3093(5)	16.5(8)	1
O3	*2i*	6162(5)	7079(5)	720(5)	17.4(8)	1
O4	*2i*	5474(5)	3022(5)	3195(5)	15.8(7)	1
O5	*2i*	9054(5)	3776(5)	2964(5)	17.3(8)	1
O6	*2i*	6930(5)	905(5)	675(5)	17.2(8)	1
O7	*2i*	2972(4)	5316(5)	3223(5)	14.9(7)	1
O8	*2i*	2860(5)	8931(5)	3658(5)	16.8(8)	1
O9	*2i*	690(5)	6596(5)	905(4)	16.5(8)	1
H9	*2i*	269.03	5538.96	499.89	25	0.5
			$Rb_2Ga(IO_3)_4(H_{0.5}IO_3)_2$			
Rb1	*2i*	8371(2)	8238(2)	3435(2)	21.6(4)	1
Al1	1*f*	5000	5000	10000	11.1(5)	1
I1	*2i*	3368.1(13)	7079.8(14)	6440.1(13)	12.0(3)	1
I2	*2i*	6920.7(13)	1477.6(13)	8309.6(13)	11.7(3)	1
I3	*2i*	8667.7(14)	6602.9(14)	8125.6(14)	14.2(3)	1
O1	*2i*	3291(15)	5676(16)	8157(16)	16(2)	1
O2	*2i*	3879(17)	9216(17)	7936(15)	20(3)	1
O3	*2i*	962(16)	6873(19)	5888(18)	23(3)	1
O4	*2i*	5437(17)	3160(16)	8138(16)	18(3)	1
O5	*2i*	6900(17)	767(16)	5965(17)	19(3)	1
O6	*2i*	9008(17)	2994(18)	8860(20)	25(3)	1
O7	*2i*	7019(16)	6723(17)	9665(16)	19(3)	1
O8	*2i*	7155(17)	6329(16)	6118(17)	20(3)	1
O9	*2i*	9270(18)	9086(17)	8418(18)	25(3)	1
H9	*2i*	9706.33	9484.25	9453.61	37	0.5

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

Table S2. Selected Bond Lengths (Å) and Bond Angles (°) of $A_2M(IO_3)_4(H_{0.5}IO_3)_2$ (A=K, Rb; M=Al, Ga).

$K_2Al(IO_3)_4(H_{0.5}IO_3)_2$		$Rb_2Al(IO_3)_4(H_{0.5}IO_3)_2$		$K_2Ga(IO_3)_4(H_{0.5}IO_3)_2$		$Rb_2Ga(IO_3)_4(H_{0.5}IO_3)_2$	
Bond	Dist. (Å)	Bond	Dist. (Å)	Bond	Dist. (Å)	Bond	Dist. (Å)
Al1–O1×2	1.893(4)	Al1–O1×2	1.910(4)	Ga1–O1×2	1.994(3)	Ga1–O1×2	1.987(11)
Al1–O4×2	1.914(4)	Al1–O4×2	1.895(4)	Ga1–O4×2	1.950(3)	Ga1–O4 ×2	1.935(11)
Al1–O7×2	1.908(4)	Al1–O7×2	1.921(4)	Ga1–O7×2	1.979(3)	Ga1–O7 ×2	1.968(12)
I1–O1	1.835(4)	I1–O1	1.838(4)	I1–O1	1.835(3)	I1–O1	1.832(12)
I1–O2	1.823(4)	I1–O2	1.793(4)	I1–O2	1.799(3)	I1–O2	1.813(13)
I1–O3	1.791(4)	I1–O3	1.802(4)	I1–O3	1.806(3)	I1–O3	1.818(12)
I2–O4	1.844(4)	I2–O4	1.832(4)	I2–O4	1.842(3)	I2–O4	1.831(11)
I2–O5	1.807(4)	I2–O5	1.791(4)	I2–O5	1.815(3)	I2–O5	1.798(13)
I2–O6	1.803(4)	I2–O6	1.829(4)	I2–O6	1.793(3)	I2–O6	1.812(13)
I3–O7	1.829(4)	I3–O7	1.824(4)	I3–O7	1.831(3)	I3–O7	1.830(12)
I3–O8	1.797(4)	I3–O8	1.795(4)	I3–O8	1.795(3)	I3–O8	1.782(13)

I3–O9	1.860(4)	I3–O9	1.859(4)	I3–O9	1.859(3)	I3–O9	1.870(13)
K1–O1	2.932(4)	Rb1–O1	3.154(4)	K1–O1	3.038(4)	Rb1–O1	3.098(12)
K1–O2	2.834(4)	Rb1–O2	3.021(4)	K1–O2	2.923(4)	Rb1–O2	2.992(13)
K1–O3	2.851(4)	Rb1–O3	2.979(4)	K1–O3	2.901(4)	Rb1–O3	2.972(13)
K1–O4	3.074(4)	Rb1–O4	3.024(4)	K1–O4	2.919(4)	Rb1–O4	3.006(13)
K1–O5	2.941(4)	Rb1–O5	2.956(4)	K1–O5	2.852(4)	Rb1–O5	2.947(12)
K1–O6	2.879(4)	Rb1–O6	3.553(4)	K1–O6	2.832(4)	Rb1–O6	3.555(13)
K1–O7	2.862(4)	Rb1–O7	2.940(4)	K1–O7	2.845(4)	Rb1–O7	2.967(14)
K1–O8	2.776(4)	Rb1–O8	2.953(4)	K1–O8	2.785(4)	Rb1–O8	2.957(12)
K1–O9	3.247(4)	Rb1–O9	2.875(4)	K1–O9	3.181(4)	Rb1–O9	2.886(13)
Angle	(°)	Angle	(°)	Angle	(°)	Angle	(°)
O2–I1–O1	96.75(18)	O2–I1–O1	95.34(18)	O2–I1–O1	94.42(15)	O2–I1–O1	96.8(5)
O2–I1–O3	99.65(19)	O2–I1–O3	100.7(2)	O2–I1–O3	101.68(17)	O2–I1–O3	101.6(6)
O3–I1–O1	96.26(17)	O3–I1–O1	96.59(19)	O3–I1–O1	96.40(16)	O3–I1–O1	95.0(5)
O5–I2–O4	95.34(17)	O5–I2–O4	96.63(18)	O5–I2–O4	96.55(16)	O5–I2–O4	97.1(5)
O5–I2–O6	101.32(19)	O5–I2–O6	99.2(2)	O5–I2–O6	99.70(16)	O5–I2–O6	100.4(6)
O6–I2–O4	96.29(18)	O6–I2–O4	96.73(18)	O6–I2–O4	96.16(16)	O6–I2–O4	97.6(6)
O7–I3–O9	93.61(17)	O7–I3–O9	94.17(18)	O7–I3–O9	93.52(16)	O7–I3–O9	93.9(6)
O8–I3–O7	96.71(17)	O8–I3–O7	97.32(18)	O8–I3–O7	96.88(16)	O8–I3–O7	97.4(6)
O8–I3–O9	97.37(18)	O8–I3–O9	96.08(19)	O8–I3–O9	96.91(16)	O8–I3–O9	96.9(6)

Table S3. The calculated bond-valence sums for each atoms of $A_2M(IO_3)_4(H_{0.5}IO_3)_2$ (A=K, Rb; M=Al, Ga).

$K_2Al(IO_3)_4(H_{0.5}IO_3)_2$		$Rb_2Al(IO_3)_4(H_{0.5}IO_3)_2$		$K_2Ga(IO_3)_4(H_{0.5}IO_3)_2$		$Rb_2Ga(IO_3)_4(H_{0.5}IO_3)_2$	
atoms	BVS	atoms	BVS	atoms	BVS	atoms	BVS
K1	1.09	Rb1	1.18	K1	1.11	Rb1	1.26
Al1	3.02	Al1	2.99	Ga1	3.10	Ga1	3.20
I1	4.87	I1	5.01	I1	4.97	I1	4.87
I2	4.97	I2	4.92	I2	4.93	I2	4.97
I3	4.81	I3	4.81	I3	4.78	I3	4.81
O1	-2.21	O1	-2.14	O1	-2.14	O1	-2.18
O2	-1.81	O2	-1.88	O2	-1.84	O2	-1.80
O3	-1.78	O3	-1.85	O3	-1.81	O3	-1.78
O4	-2.15	O4	-2.22	O4	-2.20	O4	-2.29
O5	-1.84	O5	-1.91	O5	-1.79	O5	-1.88
O6	-1.79	O6	-1.62	O6	-1.90	O6	-1.81
O7	-2.22	O7	-2.25	O7	-2.23	O7	-2.26
O8	-1.98	O8	-1.90	O8	-1.91	O8	-1.99
O9	-1.47	O9	-1.66	O9	-1.52	O9	-1.51

Table S4. Calculated bond orders of M-O, I-O, and A-O bonds of $HA_2MI_6O_{18}$ (A=K, Rb; M=Al, Ga).

$K_2Al(IO_3)_4(H_{0.5}IO_3)_2$		$Rb_2Al(IO_3)_4(H_{0.5}IO_3)_2$		$K_2Ga(IO_3)_4(H_{0.5}IO_3)_2$		$Rb_2Ga(IO_3)_4(H_{0.5}IO_3$	
bond	Bond order	bond	Bond order	Bond	Bond order	Bond	Bond order
Al1-O1	0.35	Al1-O1	0.33	Ga1-O1	0.33	Ga1-	0.34
Al1-O4	0.32	Al1-O4	0.35	Ga1-O4	0.38	Ga1-	0.38
Al1-O7	0.35	Al1-O7	0.35	Ga1-O7	0.36	Ga1-	0.37
I1 – O1	0.26	I1 – O1	0.23	I1 – O1	0.23	I1–O1	0.22
I1 – O2	0.38	I1 – O2	0.45	I1 – O2	0.44	I1–O2	0.35
I1 – O3	0.43	I1 – O3	0.37	I1 – O3	0.35	I1–O3	0.45
I2 – O4	0.24	I2 – O4	0.24	I1 – O1	0.23	I2–O4	0.21
I2 – O5	0.44	I2 – O5	0.44	I2 – O5	0.34	I2–O5	0.43
I2 – O6	0.40	I2 – O6	0.35	I2 – O6	0.43	I2–O6	0.33
I3 – O7	0.22	I3 – O7	0.21	I3 – O8	0.34	I3–O7	0.20
I3 – O8	0.38	I3 – O8	0.35	I3 – O8	0.34	I3–O8	0.34
I3 – O9	0.50	I3 – O9	0.49	I3 – O9	0.47	I3–O9	0.48
K1 – O1	0.05	Rb1–O1	0.05	K1 – O1	0.06	Rb1–	0.06
K1 – O2	0.12	Rb1–O2	0.08	K1 – O2	0.08	Rb1–	0.10
K1 – O3	0.08	Rb1–O3	0.10	K1 – O3	0.11	Rb1–	0.08
K1 – O4	0.05	Rb1–O4	0.04	K1 – O4	0.06	Rb1–	0.05
K1 – O5	0.08	Rb1–O5	0.07	K1 – O5	0.10	Rb1–	0.05
K1 – O6	0.11	Rb1–O6	0.05	K1 – O6	0.07	Rb1–	0.05
K1 – O7	0.07	Rb1–O7	0.10	K1 – O7	0.07	Rb1–	0.09
K1 – O8	0.12	Rb1–O8	0.06	K1 – O8	0.11	Rb1–	0.06
K1 – O9	0.04	Rb1–O9	0.10	K1 – O9	0.04	Rb1–	0.10

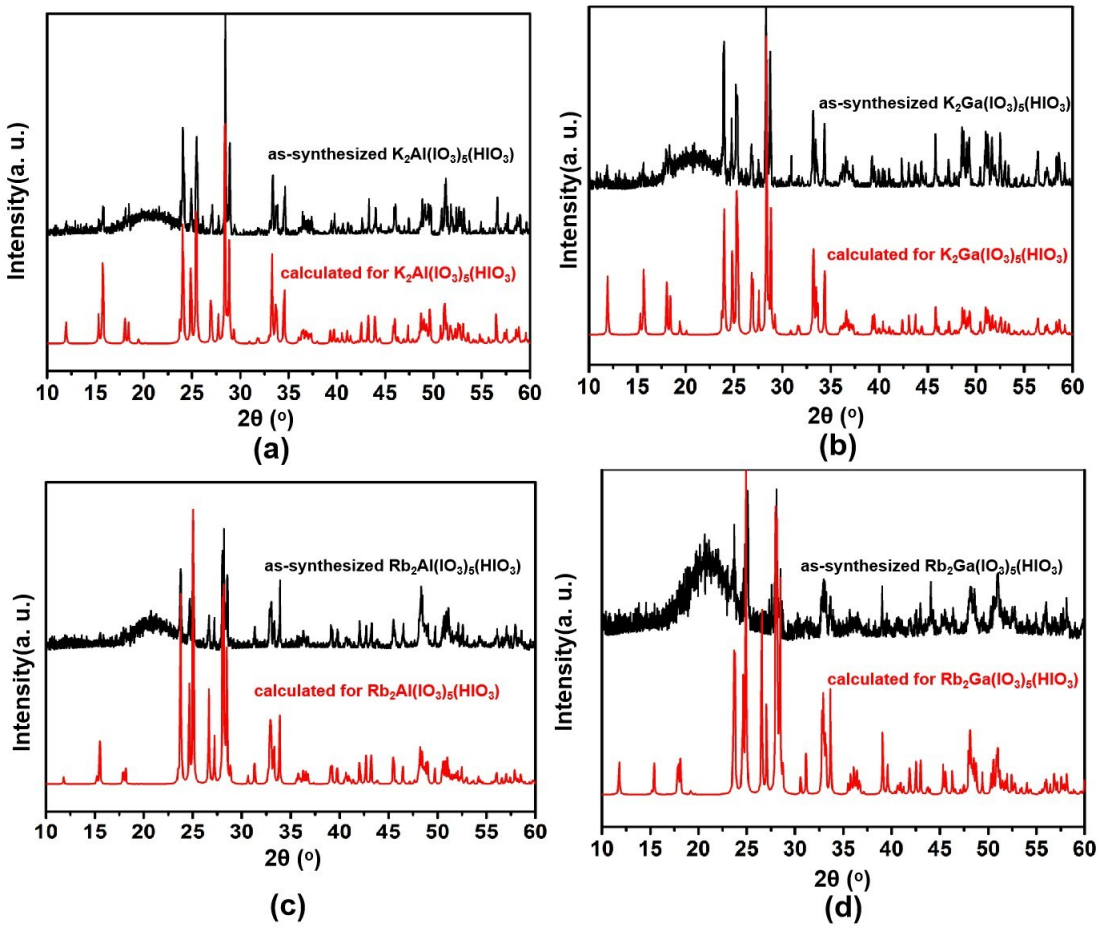

Figure S1. XRD patterns of as-synthesized samples compare with single crystal simulated models of $K_2Al(IO_3)_4(H_{0.5}IO_3)_2$ (a), $Rb_2Al(IO_3)_4(H_{0.5}IO_3)_2$ (b), $K_2Ga(IO_3)_4(H_{0.5}IO_3)_2$ (c), and $Rb_2Ga(IO_3)_4(H_{0.5}IO_3)_2$ (d).

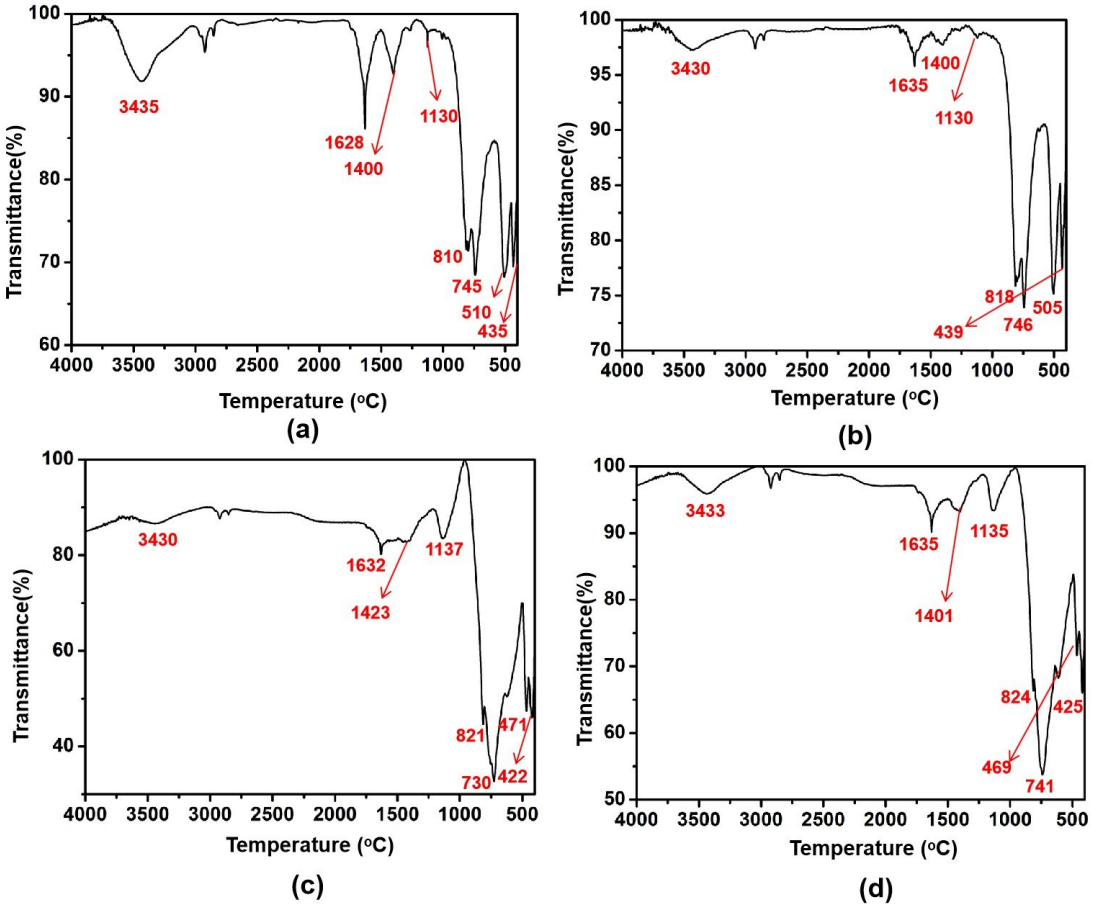

Figure S2. IR spectra of $K_2Al(IO_3)_4(H_{0.5}IO_3)_2$ (a), $Rb_2Al(IO_3)_4(H_{0.5}IO_3)_2$ (b), $K_2Ga(IO_3)_4(H_{0.5}IO_3)_2$ (c), and $Rb_2Ga(IO_3)_4(H_{0.5}IO_3)_2$ (d).

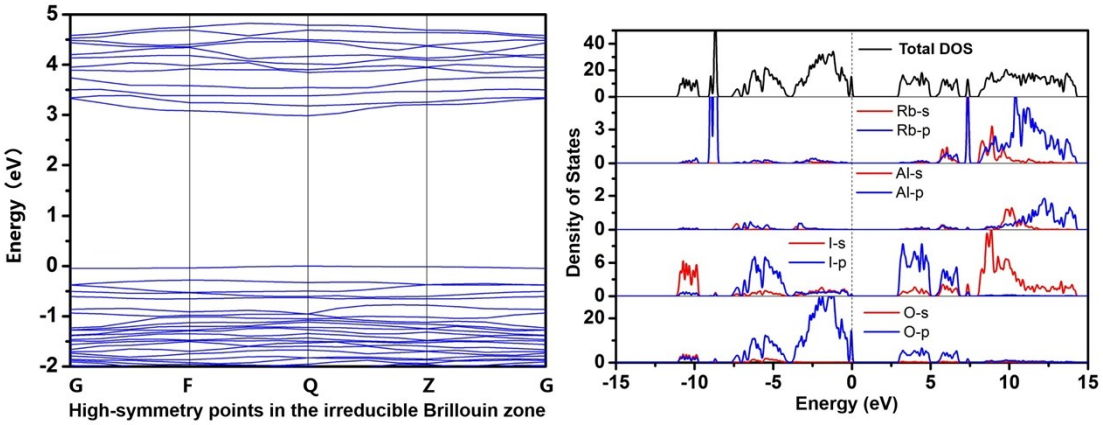

Figure S3. Calculated electronic band structure (left) and total and partial densities of states of $Rb_2Al(IO_3)_4(H_{0.5}IO_3)_2$ (right).

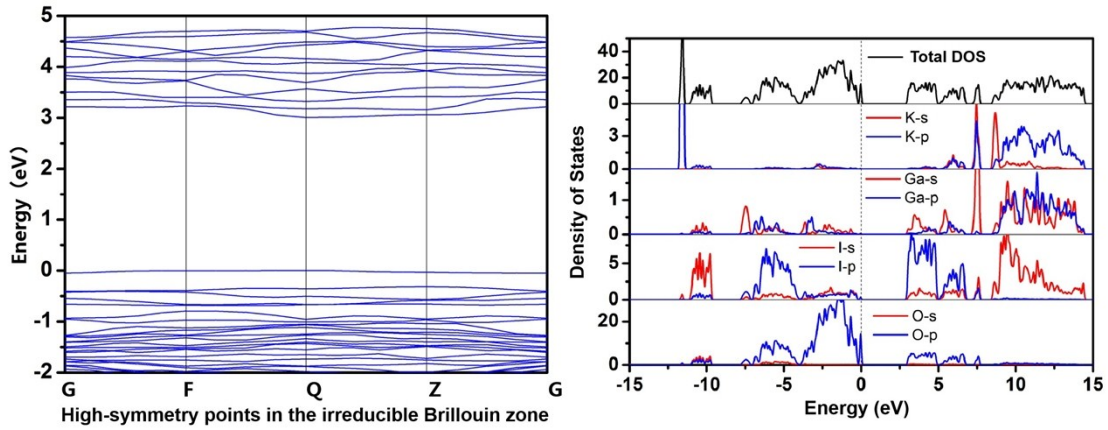

Figure S4. Calculated electronic band structure (left) and total and partial densities of states of $K_2Ga(IO_3)_4(H_{0.5}IO_3)_2$ (right).

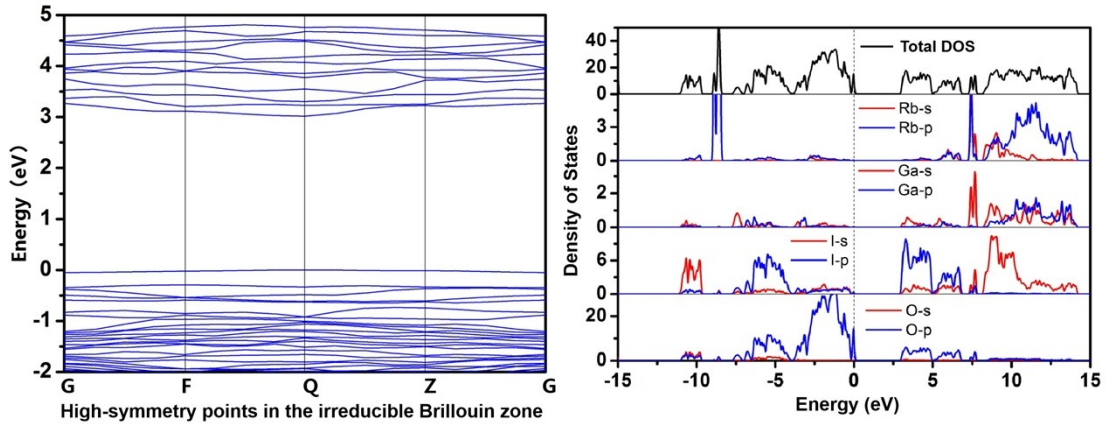

Figure S5. Calculated electronic band structure (left) and total and partial densities of states of $Rb_2Ga(IO_3)_4(H_{0.5}IO_3)_2$ (right).