$Ag_3I[(MoO_3)_2(IO_3)_2]$: A New Polar Material from the Structural Modulation of Molybdenyl Iodate Architectures by polarizable Cation (Ag^+) and Anion (I^-)

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Electronic Supplementary Information

Table S1 Atomic coordinates ($Å\times10^{-4}$) and equivalent isotropic displacement parameters ($Å^2\times10^{-3}$) for $Ag_3I[(MoO_3)_2(IO_3)_2]$.

atom	Wyckoff	x	y	z	U(eq)[a]
I(1)	4a	6413(1)	2623(1)	3681(1)	10(1)
I(2)	4a	6826(1)	2819(1)	-1338(1)	11(1)
I(3)	4a	8747(1)	2(1)	2956(1)	21(1)
Mo(1)	4a	4880(1)	1226(1)	5422(1)	9(1)
Mo(2)	4a	4938(1)	1238(1)	417(1)	10(1)
Ag(1)	4a	10005(1)	980(1)	5404(1)	28(1)
Ag(2)	4a	12168(1)	-62(1)	2889(1)	29(1)
Ag(3)	4a	9883(1)	1017(1)	927(1)	33(1)
O(1)	4a	5265(6)	1526(2)	2878(8)	13(1)
O(2)	4a	4102(6)	1345(2)	7879(8)	12(1)
O(3)	4a	5114(7)	3342(3)	-1799(9)	21(1)
O(4)	4a	7402(7)	3263(3)	4969(7)	14(1)
O(5)	4a	5771(8)	2210(3)	5797(7)	15(1)
O(6)	4a	3843(8)	561(3)	4810(8)	18(1)
O(7)	4a	6835(9)	961(3)	5921(8)	20(2)
O(8)	4a	4481(7)	3037(3)	3303(8)	19(1)
O(9)	4a	5660(9)	2243(3)	-30(8)	23(2)

O(10)	4a	3959(9)	555(3)	929(8)	19(1)
O(11)	4a	6911(8)	1001(4)	-193(8)	22(2)
O(12)	4a	7502(8)	3246(3)	753(7)	16(1)

[a]U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table S2 Selected bond distances (Å) for $Ag_3I[(MoO_3)_2(IO_3)_2]$.

Bond	Distance	Bond	Distance
I(1)-O(8)	1.802(5)	Ag(1)-O(7)	2.566(7)
I(1)-O(4)	1.836(6)	Ag(1)-O(8)	2.628(5)
I(1)-O(5)	1.854(6)	Ag(1)-I(3)#2	2.974(1)
I(2)-O(3)	1.797(5)	Ag(1)-I(3)	2.925(1)
I(2)-O(9)	1.813(6)	Ag(2)-O(6)#7	2.352(6)
I(2)-O(12)	1.862(5)	Ag(2)-O(10)#7	2.417(6)
Mo(1)-O(6)	1.700(6)	Ag(2)-O(7)#1	2.525(6)
Mo(1)-O(7)	1.704(7)	Ag(2)-O(11)#2	2.550(7)
Mo(1)-O(2)	1.921(6)	Ag(2)- I(3)	2.743(1)
Mo(1)-O(1)	1.993(6)	Ag(3)-O(3)#6	2.424(6)
Mo(1)-O(5)	2.227(6)	Ag(3)-O(11)	2.517(7)
Mo(1)-O(4)#3	2.286(6)	Ag(3)-O(12)	2.619(5)
Mo(2)-O(10)	1.693(7)	Ag(3)-O(8)	2.678(4)
Mo(2)-O(11)	1.718(6)	I(3)-Ag(3)	2.775(1)
Mo(2)-O(1)	1.922(6)	I(3)-Ag(3)#2	3.261(1)
Mo(2)-O(2)#4	1.989(6)	Ag(1)-Ag(2)#2	3.186(1)
Mo(2)-O(9)	2.239(6)	Ag(1)-Ag(3)	3.282(1)
Mo(2)-O(12)#3	2.251(7)	Ag(1)-Ag(2)	3.362(1)
Ag(1)-O(3)#5	2.507(6)	Ag(2)-Ag(3)	3.268(1)

Ag(1)-O(4)#6	2.526(6)	

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y,z-1/2 , #2 -x+2,-y,z+1/2 , #3 x-1/2,-y+1/2,z , #4 x,y,z-1, #5 x+1/2,-y+1/2,z+1, #6 x+1/2,-y+1/2,z, #7 x+1,y,z .

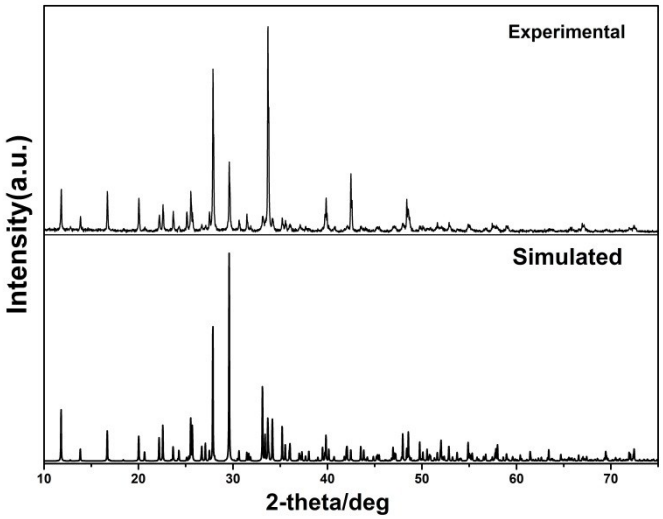

Fig. S1 Experimental and simulated powder X-ray diffraction patterns for $Ag_3I[(MoO_3)_2(IO_3)_2]$ synthesized from a mixture of $AgNO_3$ (0.5mmol), MoO_3 (0.5mmol) , I_2O_5 (0.75mmol), TeO_2 (1mmol) and H_2O (3ml).

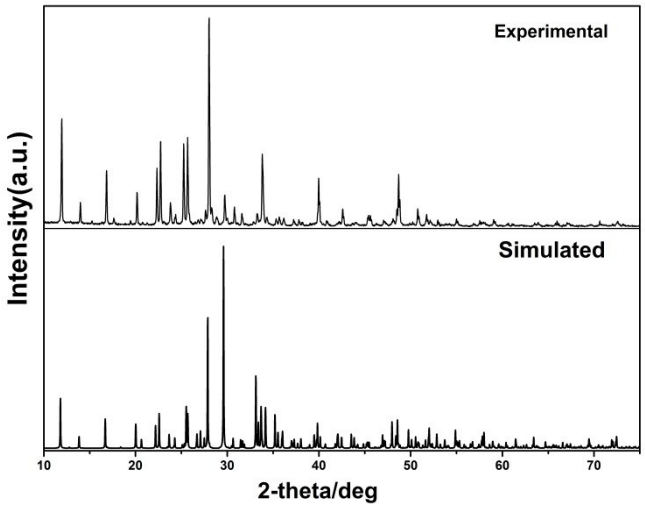

Fig. S2 Experimental and simulated powder X-ray diffraction patterns for $Ag_3I[(MoO_3)_2(IO_3)_2]$ synthesized from a mixture of $AgNO_3$ (2mmol), MoO_3 (2mmol) , KIO_3 (2mmol), AgI (1mmol) and H_2O (6ml).

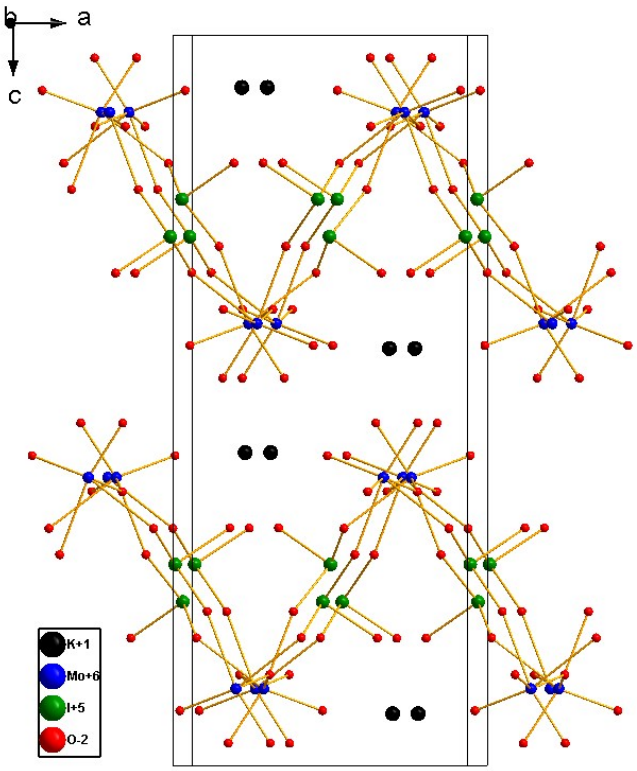

Fig. S3 Crystal structure of α-$K_2[(MoO_3)_2(IO_3)_2]$ viewed along [001].

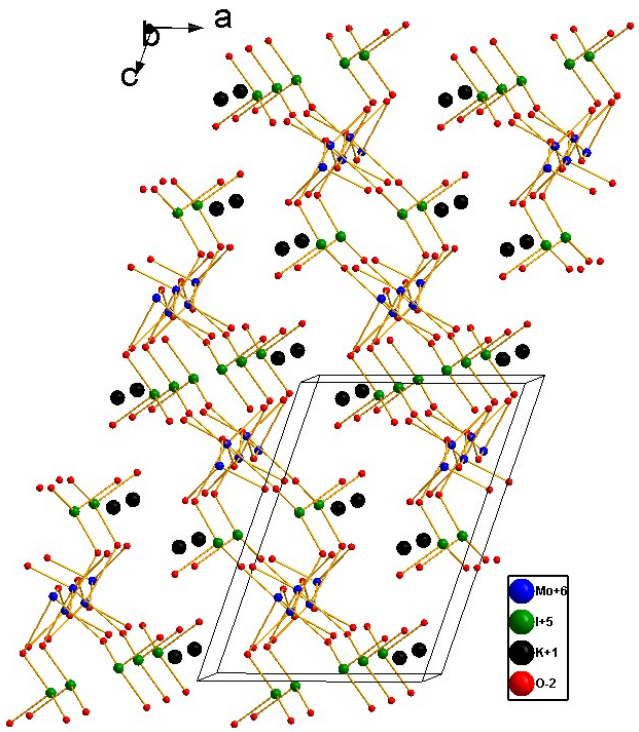

Fig. S4 Crystal structure of β-$K_2[(MoO_3)_2(IO_3)_2]$ viewed along [001].

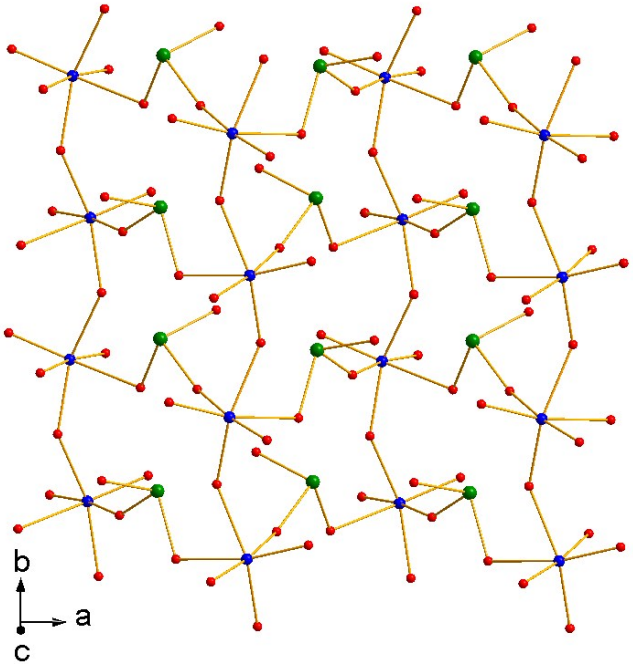

Fig. S5 2D $[(MoO_3)_2(IO_3)_2]_\infty^{2n+}$ anionic layer viewed along *b* axis for α-$K_2[(MoO_3)_2(IO_3)_2]$ and the bridging iodate anions alternately align in an opposite direction manner along *b* axis.

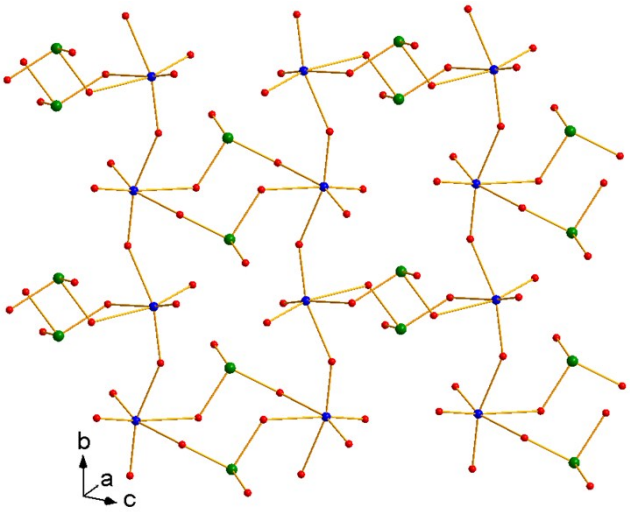

Fig. S6 2D $[(MoO_3)_2(IO_3)_2]_\infty^{2n+}$ anionic layer viewed along *b* axis for β-$K_2[(MoO_3)_2(IO_3)_2]$ and the bridging iodate anions alternately align in an opposite direction manner along *b* axis.

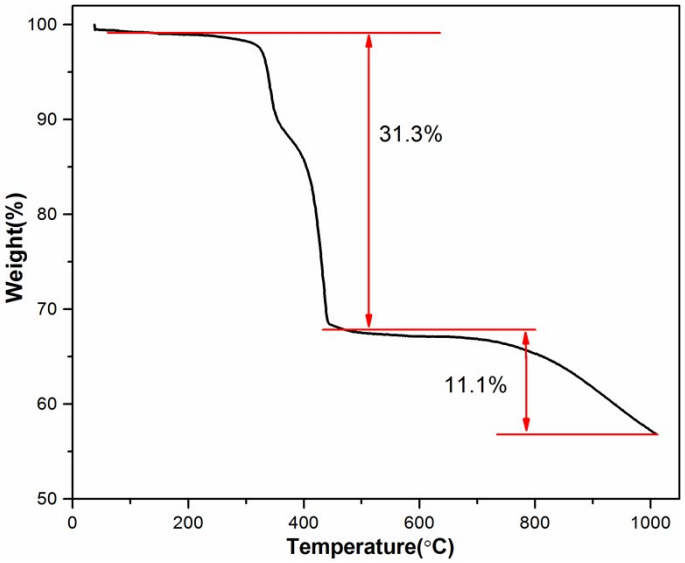

Fig. S7 Plot of thermogravimetric (TGA) vs. temperature for compound $Ag_3I[(MoO_3)_2(IO_3)_2]$.

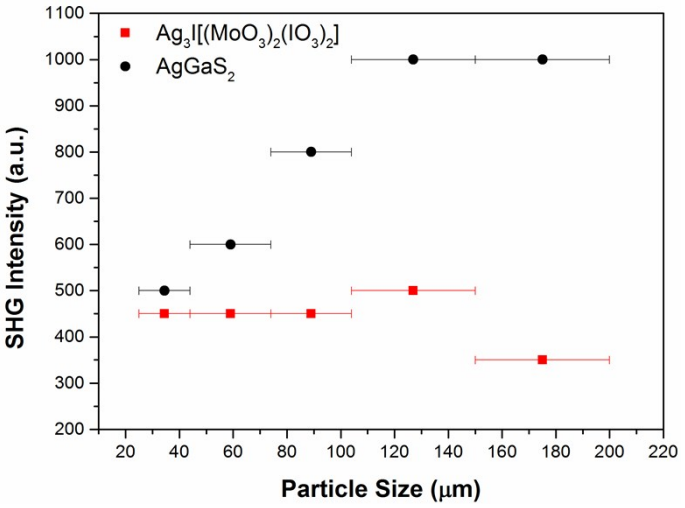

Fig. S8 Particle size vs. SHG intensity for $Ag_3I[(MoO_3)_2(IO_3)_2]$ and $AgGaS_2$ references.