Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Electronic Supplementary Information

$A_2BiI_5O_{15}$ (A=K^+ or Rb^+): Two New Promising Nonlinear Optical Materials Containing $[I_3O_9]^{3-}$ Bridging Anionic Group †

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1. XRD and EDX of $K_2BiI_5O_{15}$ and $Rb_2BiI_5O_{15}$.

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Table S1. Selected Bond Distances (Å) for $K_2BiI_5O_{15}$.

Table S2. Selected Bond Distances (Å) for $Rb_2BiI_5O_{15}$.

1. XRD and EDX of $K_2BiI_5O_{15}$ and $Rb_2BiI_5O_{15}$.

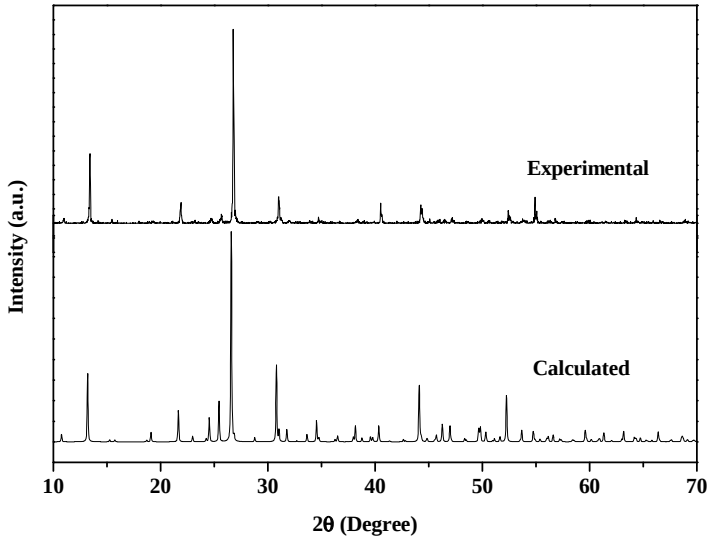

Figure S1. Calculated and experimental powder XRD patterns of $K_2BiI_5O_{15}$.

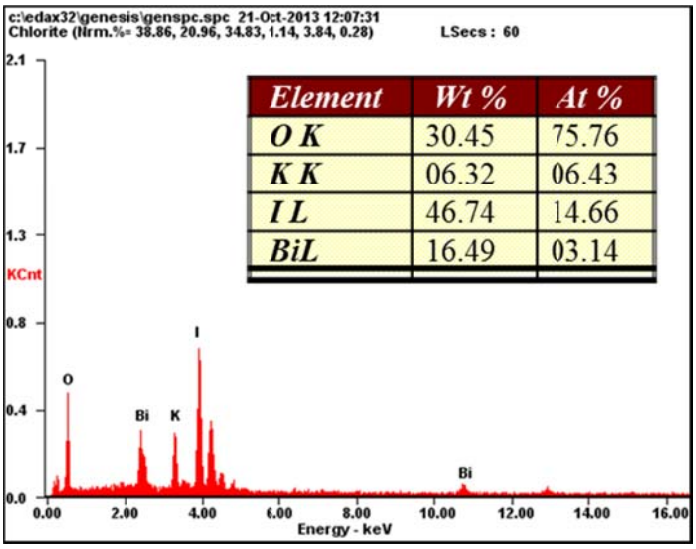

Figure S2. EDX of $K_2BiI_5O_{15}$.

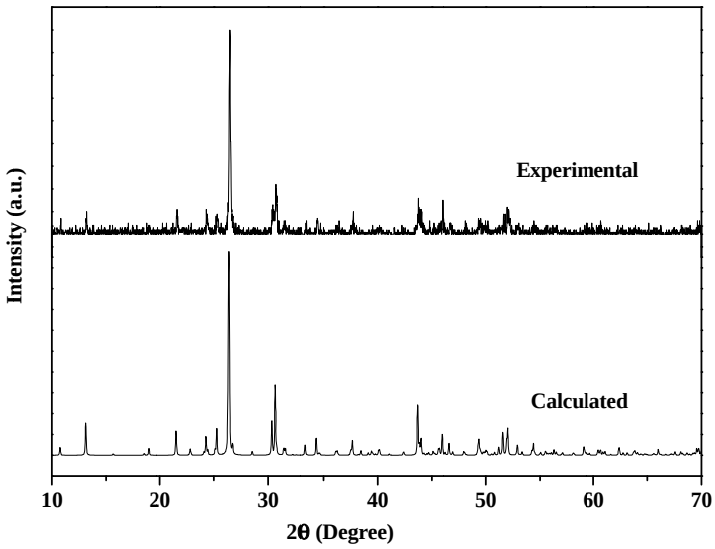

Figure S3. Calculated and experimental powder XRD patterns of $Rb_2BiI_5O_{15}$.

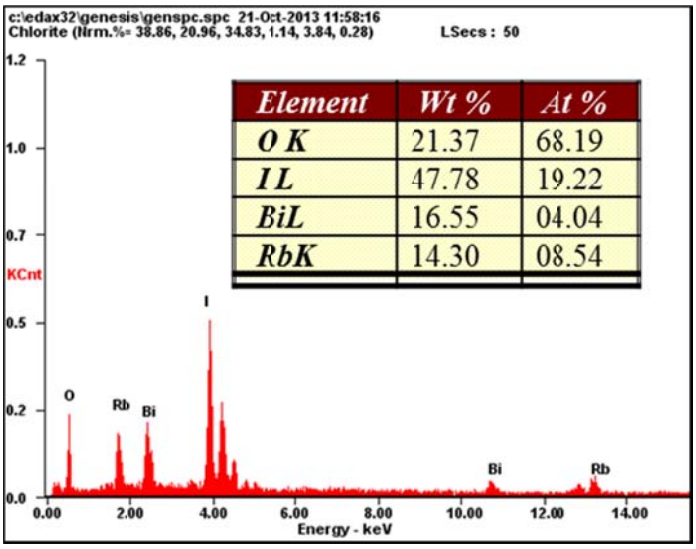

Figure S4. EDX of $Rb_2BiI_5O_{15}$.

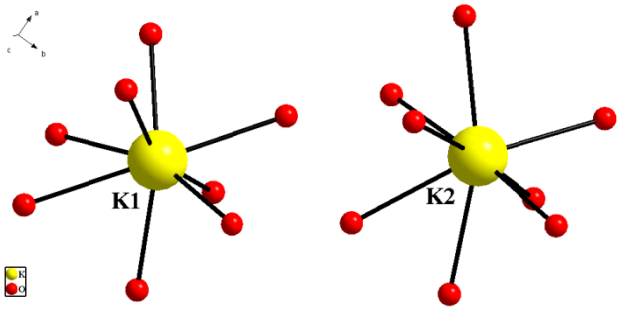

Figure S5. The coordination structure of K atoms in $K_2BiI_5O_{15}$.

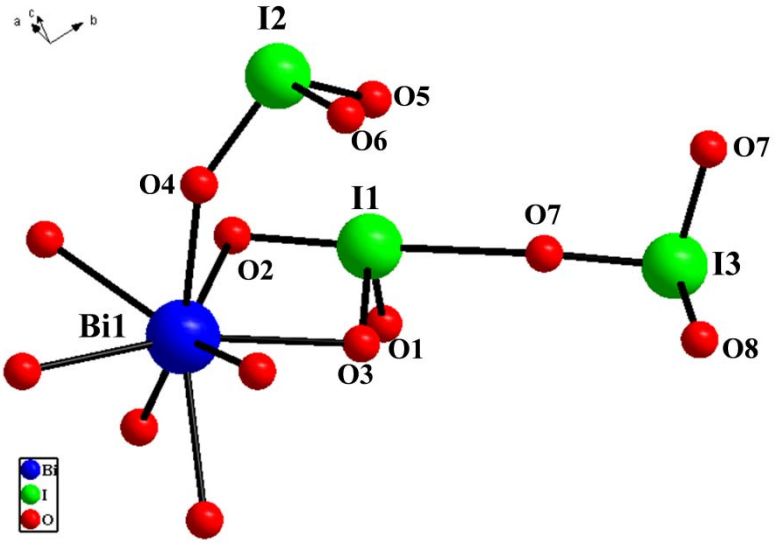

Figure S6. The coordination structure of Bi and I atoms in $K_2BiI_5O_{15}$.

2. ATR-FTIR Spectra of $K_2BiI_5O_{15}$ and $Rb_2BiI_5O_{15}$.

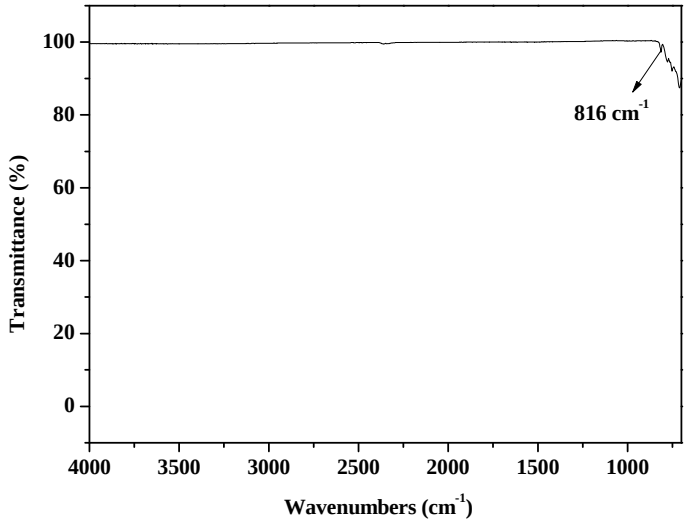

Figure S7. The ATR-FTIR spectrum of $K_2BiI_5O_{15}$.

3.

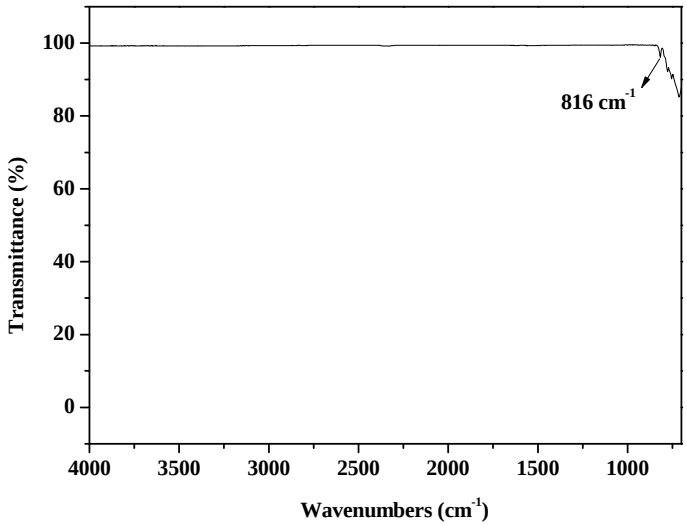

Figure S8. The ATR-FTIR spectrum of $Rb_2BiI_5O_{15}$.

3. Theoretical Computations.

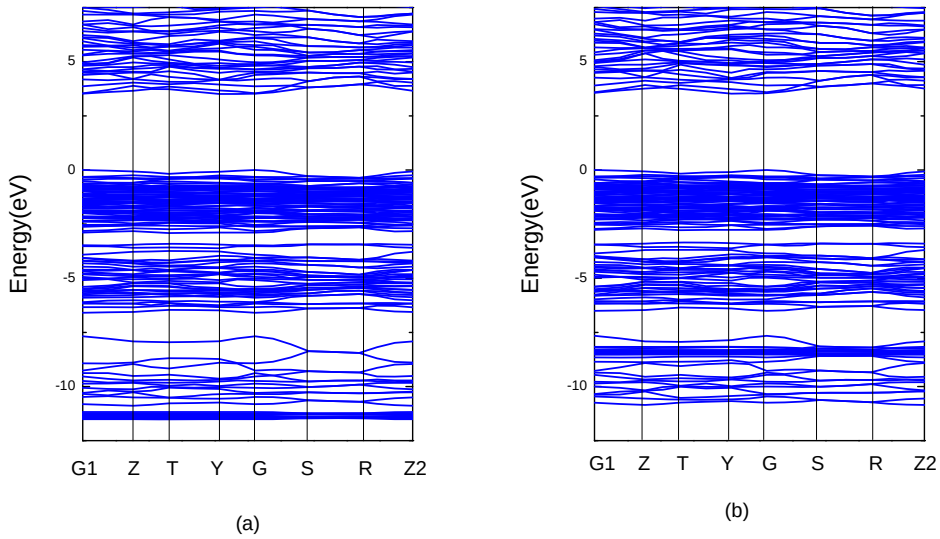

Figure S9. Electronic band structure of $K_2BiI_5O_{15}$ (a) and $Rb_2BiI_5O_{15}$ (b) crystals along the lines of high symmetry points in the Brillouin zone.

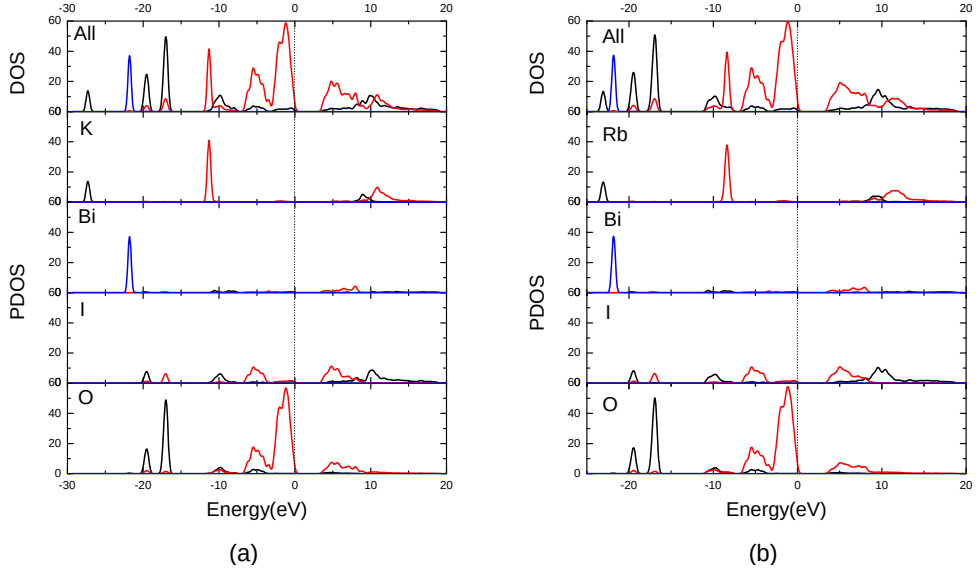

Figure S10. DOS and PDOS plots of $K_2BiI_5O_{15}$ (a) and $Rb_2BiI_5O_{15}$ (b). The *s*, *p* and *d* orbitals are represented by black, red and blue curves, respectively. The VB maximum is indicated by the dotted straight line.

4. Thermal properties of $K_2BiI_5O_{15}$ and $Rb_2BiI_5O_{15}$

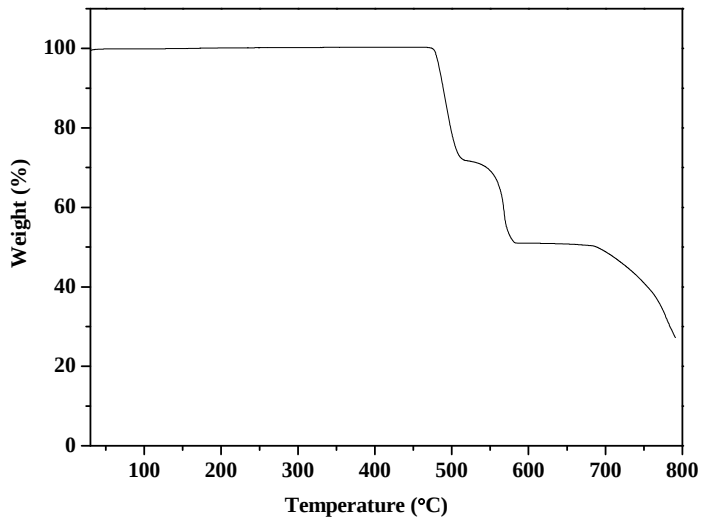

Figure S11. TGA curve of $K_2BiI_5O_{15}$.

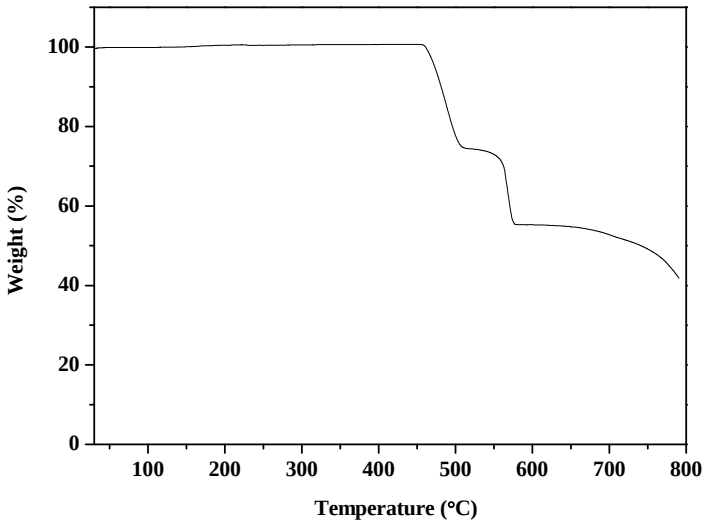

Figure S12. TGA curve of $Rb_2BiI_5O_{15}$.

Table S1. Selected Bond Distances (Å) for $K_2BiI_5O_{15}$.

Bond	Bond distances	Bond	Bond distances
Bi(1)-O(4)#1	2.352(5)	K(1)-O(1)#8	2.734(5)
Bi(1)-O(4)	2.352(5)	K(1)-O(1)	2.817(5)
Bi(1)-O(2)#1	2.399(4)	K(1)-O(1)#9	2.817(5)
Bi(1)-O(2)	2.400(4)	K(1)-O(4)#1	3.040(5)

Bi(1)-O(3)	2.491(4)	K(1)-O(4)#10	3.040(5)
Bi(1)-O(3)#1	2.491(4)	K(1)-O(3)#9	3.127(5)
Bi(1)-O(2)#2	2.549(4)	K(1)-O(3)	3.127(5)
Bi(1)-O(2)#3	2.549(4)	K(2)-O(5)#3	2.839(5)
I(1)-O(1)	1.797(4)	K(2)-O(5)#11	2.839(5)
I(1)-O(3)	1.829(5)	K(2)-O(5)	2.896(6)
I(1)-O(2)	1.865(4)	K(2)-O(5)#7	2.896(6)
I(1)-O(7)	2.457(5)	K(2)-O(6)	3.067(6)
I(2)-O(6)	1.803(5)	K(2)-O(6)#7	3.067(6)
I(2)-O(5)	1.808(4)	K(2)-O(7)	3.108(6)
I(2)-O(4)	1.822(5)	K(2)-O(7)#7	3.108(6)
I(3)-O(7)#7	1.790(5)	O(1)-K(1)#5	2.734(5)
I(3)-O(7)	1.790(5)	O(2)-Bi(1)#5	2.549(4)
I(3)-O(8)	1.815(7)	O(4)-K(1)#4	3.040(5)
K(1)-O(1)#2	2.734(5)	O(5)-K(2)#6	2.839(5)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,z #2 x,-y+0,z-1/2 #3 -x+1,y+0,z-1/2 #4 x+1,y,z

#5 x,-y+0,z+1/2 #6 -x+1,-y+1/2,z+1/2 #7 x,-y+1/2,z #8 -x,y+0,z-1/2

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

Table S2. Selected Bond Distances (Å) for $Rb_2BiI_5O_{15}$.

Bond	Bond distances	Bond	Bond distances
Bi(1)-O(2)	2.368(9)	Rb(1)-O(1)#9	2.917(9)
Bi(1)-O(2)#1	2.368(9)	Rb(1)-O(1)	2.917(9)
Bi(1)-O(4)#1	2.371(9)	Rb(1)-O(4)#1	3.050(10)
Bi(1)-O(4)	2.371(9)	Rb(1)-O(4)#10	3.050(10)
Bi(1)-O(3)#1	2.503(8)	Rb(1)-O(3)#9	3.235(9)
Bi(1)-O(3)	2.504(8)	Rb(1)-O(3)	3.235(9)
Bi(1)-O(2)#2	2.631(9)	Rb(1)-O(2)#8	3.589(9)
Bi(1)-O(2)#3	2.631(9)	Rb(1)-O(2)#2	3.589(9)
I(1)-O(1)	1.799(8)	Rb(2)-O(5)#3	2.903(10)
I(1)-O(3)	1.832(10)	Rb(2)-O(5)#11	2.903(10)
I(1)-O(2)	1.865(8)	Rb(2)-O(5)#7	3.019(11)
I(1)-O(7)	2.452(13)	Rb(2)-O(5)	3.019(11)
I(2)-O(6)	1.800(11)	Rb(2)-O(6)#7	3.133(11)
I(2)-O(5)	1.801(8)	Rb(2)-O(6)	3.133(11)
I(2)-O(4)	1.825(9)	Rb(2)-O(7)	3.186(14)

I(3)-O(7)	1.799(12)	Rb(2)-O(7)#7	3.186(14)
I(3)-O(7)#7	1.799(12)	O(1)-Rb(1)#5	2.822(10)
I(3)-O(8)	1.82(2)	O(2)-Bi(1)#5	2.631(9)
Rb(1)-O(1)#2	2.822(10)	O(4)-Rb(1)#4	3.050(10)
Rb(1)-O(1)#8	2.822(10)	O(5)-Rb(2)#6	2.903(10)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,z #2 x,-y+0,z-1/2 #3 -x+1,y+0,z-1/2 #4 x+1,y,z

#5 x,-y+0,z+1/2 #6 -x+1,-y+1/2,z+1/2 #7 x,-y+1/2,z #8 -x,y+0,z-1/2

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