$K_3V_2O_3F_4(IO_3)_3$: A High-Performance SHG Crystal Containing Both Five and Six-coordinated V^{5+} Cations

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Table S1. Selected bond distances (Å) for $K_3V_2O_3F_4(IO_3)_3$.

K(1)-F(1)	2.647(6)	V(1)-O(8)	1.576(10)
K(1)-F(1)#1	2.647(6)	V(1)-O(3)	1.872(6)
K(1)-O(2)#2	2.863(7)	V(1)-O(3)#3	1.872(6)
K(1)-O(2)#3	2.863(7)	V(1)-F(1)	1.872(5)
K(1)-O(4)#1	3.003(7)	V(1)-F(1)#3	1.872(5)
K(1)-O(4)	3.003(7)	V(1)-O(6)	2.311(9)
K(1)-O(1)#2	3.067(7)	V(2)-O(6)	1.633(9)
K(1)-O(1)#3	3.067(7)	V(2)-O(7)	1.700(9)
K(2)-F(2)#4	2.621(6)	V(2)-F(2)	1.856(6)
K(2)-F(1)	2.673(5)	V(2)-F(2)#3	1.856(6)
K(2)-F(2)#5	2.706(6)	V(2)-O(5)#7	2.032(8)
K(2)-O(1)#3	2.721(7)	I(1)-O(2)	1.782(6)
K(2)-F(1)#5	2.736(5)	I(1)-O(1)	1.791(6)
K(2)-O(4)#5	2.823(6)	I(1)-O(3)	1.882(6)
K(2)-O(6)#6	3.090(3)	I(2)-O(4)	1.819(6)
		I(2)-O(4)#3	1.819(6)
		I(2)-O(5)	1.850(8)

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

Table S2. The bond angles (°) for $V(1)O_4F_2$ octahedron and $V(2)O_3F_2$ trigonal-bipyramid.

$V(1)O_4F_2$ octahedron		$V(2)O_3F_2$ trigonal-bipyramid	
O(8)-V(1)-O(3)	101.7(3)	O(6)-V(2)-O(7)	106.7(5)
O(8)-V(1)-O(3)#1	101.7(3)	O(6)-V(2)-F(2)	101.20(18)
O(3)-V(1)-O(3)#1	94.1(4)	O(7)-V(2)-F(2)	91.3(2)
O(8)-V(1)-F(1)	99.2(3)	O(6)-V(2)-F(2)#1	101.20(18)
O(3)-V(1)-F(1)	158.2(3)	O(7)-V(2)-F(2)#1	91.3(2)
O(3)#1-V(1)-F(1)	87.6(2)	F(2)-V(2)-F(2)#1	155.7(3)
O(8)-V(1)-F(1)#1	99.2(3)	O(6)-V(2)-O(5)#2	102.9(4)
O(3)-V(1)-F(1)#1	87.6(2)	O(7)-V(2)-O(5)#2	150.3(4)
O(3)#1-V(1)-F(1)#1	158.2(3)	F(2)-V(2)-O(5)#2	82.93(19)
F(1)-V(1)-F(1)#1	83.1(3)	F(2)#1-V(2)-O(5)#2	82.93(19)
O(8)-V(1)-O(6)	178.9(4)		
O(3)-V(1)-O(6)	79.0(2)		
O(3)#1-V(1)-O(6)	79.0(2)		
F(1)-V(1)-O(6)	80.0(2)		
F(1)#1-V(1)-O(6)	80.0(2)		

Symmetry transformations used to generate equivalent atoms:
#1 -x, y, z; #2 -x, -y+1, z-1/2.

Table S3. The structure features and SHG properties of metal vanadium iodates.

Compound	Structural features	SHG efficiency	Ref[a]
$Zn_2(VO_4)(IO_3)$	isolated $(VO_4)^{3-}$ and $(IO_3)^-$ unit	6 × KDP	36
β-$Ba[VFO_2(IO_3)_2]$	0D *trans*-$[VFO_2(IO_3)_2]^{2-}$ unit	1.5 × KDP	35
α-$Ba_2[VO_2F_2(IO_3)_2]IO_3$	0D *cis*-$[VO_2F_2(IO_3)_2]^{3-}$ unit	9 × KDP	35
β-$Ba_2[VO_2F_2(IO_3)_2]IO_3$		9 × KDP	35
$LaVO_2(IO_3)_4 \cdot H_2O$	0D $[VO_2(IO_3)_4]^{3-}$ unit	0.2 × KDP	40
$K_3V_2O_4F_3(IO_3)_3$	**0D $[V_2O_4F_3(IO_3)_3]^{3-}$ unit**	**1.3 × KTP**	**This work**
$NaVO_2(IO_3)_2(H_2O)$	1D $[VO_2(IO_3)_2]^-$ chain	20 × KDP	39
$K(VO)_2O_2(IO_3)_3$	1D $[(VO)_2O_2(IO_3)_3]^-$ chain	3.6 × KTP	38
$Rb(VO)_2O_2(IO_3)_3$	1D $[(VO)_2O_2(IO_3)_3]^-$ chain	2.2 × KTP	42
$Cs(VO)_2O_2(IO_3)_3$	1D $[(VO)_2O_2(IO_3)_3]^-$ chain	1.3 × KTP	42
$(NH_4)(VO)_2O_2(IO_3)_3$	1D $[(VO)_2O_2(IO_3)_3]^-$ chain	1.2 × KTP	42
$Tl(VO)_2O_2(IO_3)_3$	1D $[(VO)_2O_2(IO_3)_3]^-$ chain	0.4 × KTP	37
$CsVO_2F(IO_3)$	3D $[VO_2F(IO_3)]^-$ framework	1.1 × KTP	34

a: The references in the table refer to those in the main text.

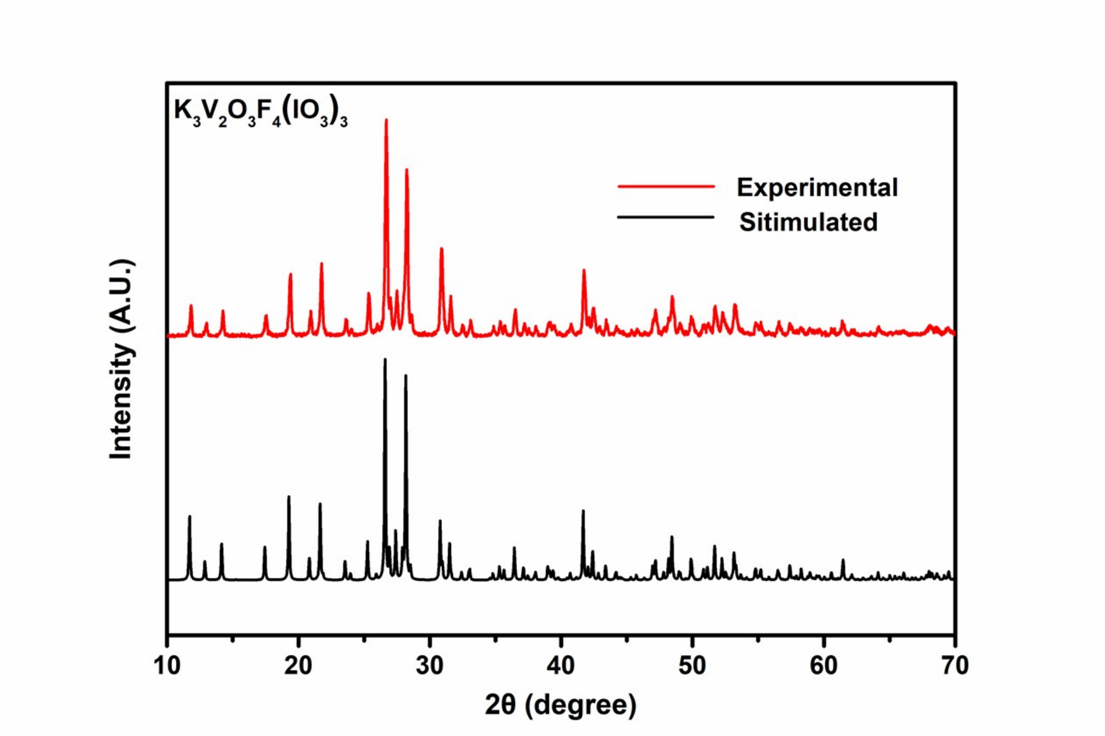
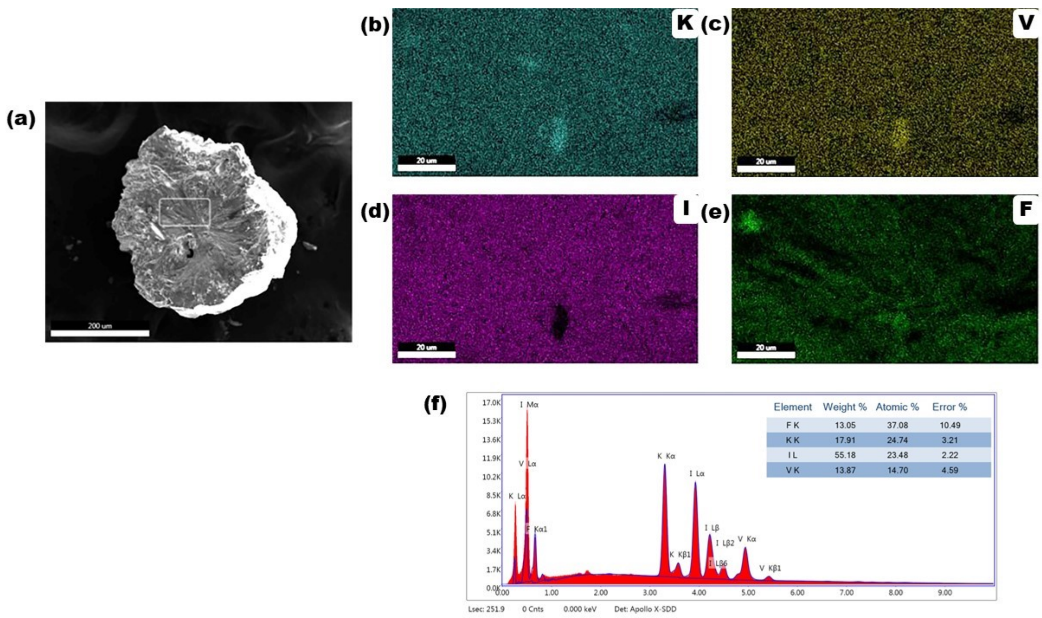


Figure S1. Simulated and measured powder X-ray diffraction patterns for $K_3V_2O_3F_4(IO_3)_3$.



Element	Weight %	Atomic %	Error %
F K	13.05	37.08	10.49
K K	17.91	24.74	3.21
I L	55.18	23.48	2.22
V K	13.87	14.70	4.59

Figure S2. SEM image of $K_3V_2O_3F_4(IO_3)_3$ (a), its elemental distribution maps (b-e) and the EDS image with quantitative analysis table (f).

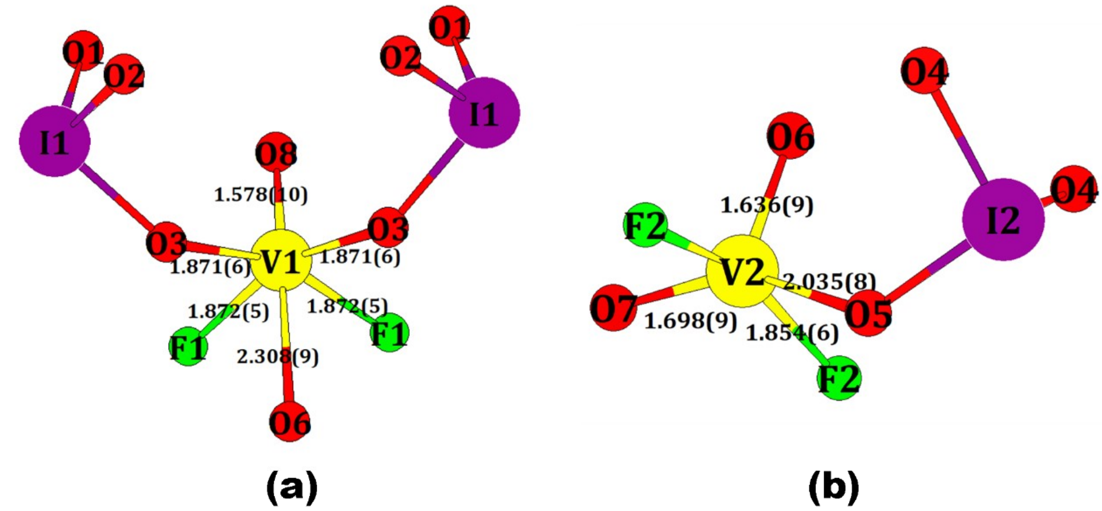


Figure S3. The coordination geometries for $V(1)^{+}$ (a) and $V(2)^{+}$ (b) cations.

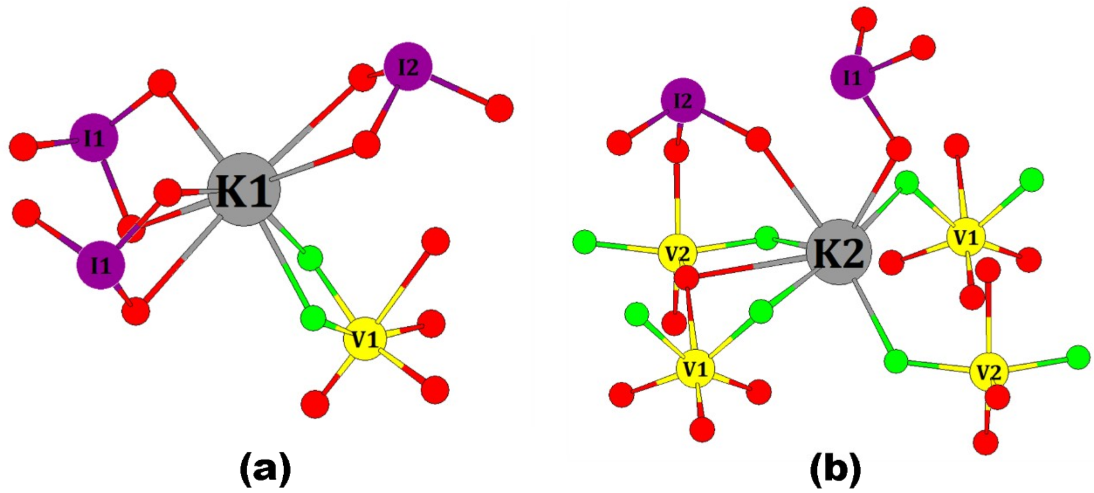


Figure S4. The coordination geometries for $K(1)^{+}$ (a) and $K(2)^{+}$ (b) cations.

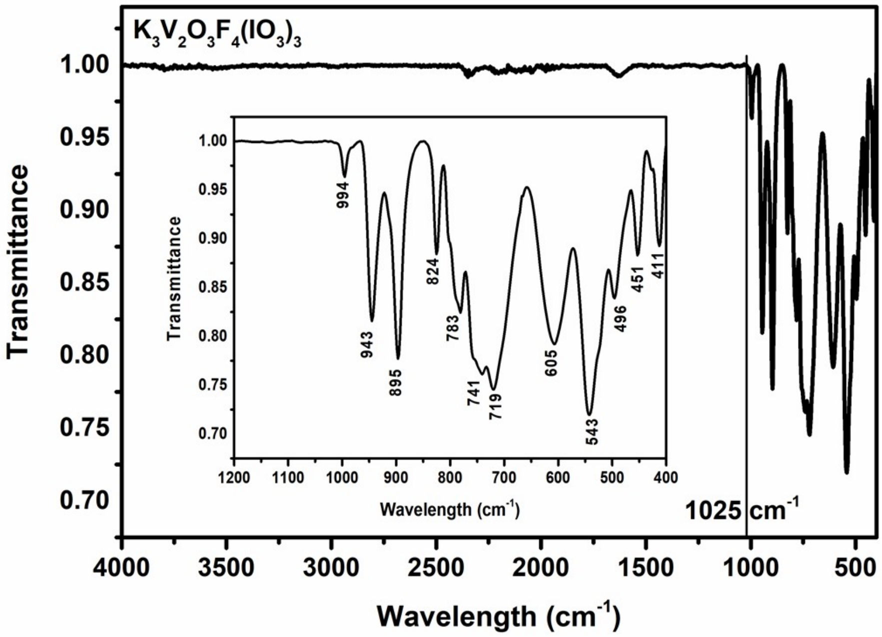


Figure S5. IR spectrum for $K_3V_2O_3F_4(IO_3)_3$.

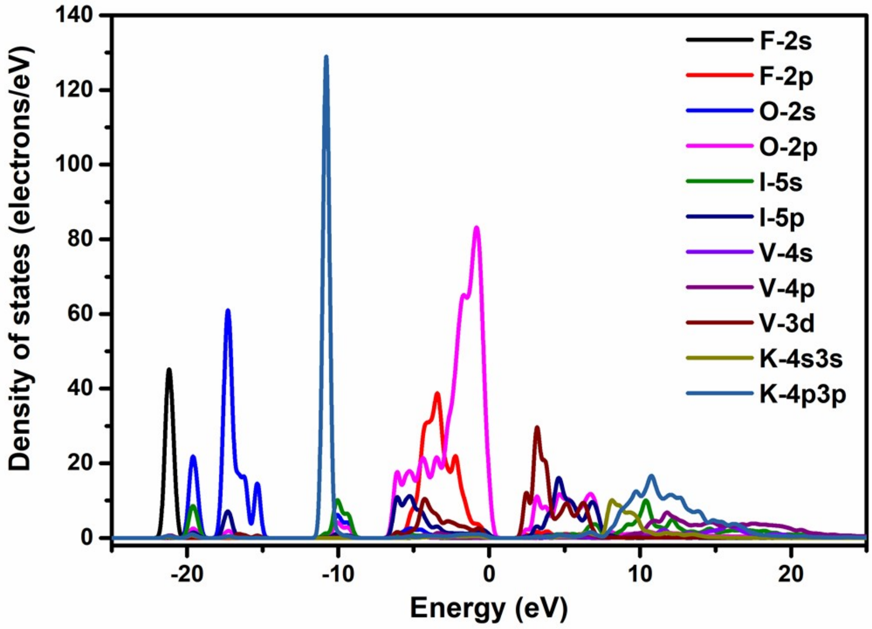


Figure S6. The scissor-added partial density of states for $K_3V_2O_3F_4(IO_3)_3$.