Supporting Information

NaMoO$_3$(IO$_3$)(H$_2$O): Water Molecule Introduction Induces Strong Second Harmonic Generation Response, Widened Band Gap and Large Anisotropy.

Contents

Table S1. Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) and BVS for $NaMoO_3(IO_3)(H_2O)$.

	x	y	z	U(eq)	BVS
I(1)	5189(2)	2668(3)	3298(2)	12(1)	5.00
I(2)	4794(2)	7669(3)	3198(2)	12(1)	5.38
Mo(1)	7678(3)	4999(3)	5652(4)	7(1)	6.14
Mo(2)	2306(3)	9980(3)	4339(4)	7(1)	6.18
Na(1)	7505(15)	-190(30)	6000(20)	47(6)	0.98
Na(2)	2479(16)	4690(30)	4690(20)	41(5)	1.01
O(1)	8870(20)	30(30)	3740(40)	23(6)	-
O(2)	1120(20)	4940(30)	6840(40)	27(6)	-
O(3)	5990(30)	600(40)	3420(30)	28(7)	1.93
O(4)	3830(20)	2110(30)	4200(30)	20(5)	2.28
O(5)	5960(20)	3420(30)	5600(30)	17(5)	2.27
O(6)	8630(20)	3320(30)	6260(30)	22(5)	1.86
O(7)	7240(20)	5620(30)	8050(30)	15(5)	1.82
O(8)	8700(20)	6610(30)	5580(40)	32(6)	1.88
O(9)	6110(20)	7120(30)	4680(40)	27(6)	2.58
O(10)	3980(30)	5640(30)	2870(40)	31(7)	2.01
O(11)	4020(20)	8420(30)	5150(30)	21(5)	1.88
O(12)	1360(20)	8290(30)	4480(30)	24(6)	1.85
O(13)	1280(20)	11600(30)	3780(40)	28(6)	1.86
O(14)	2760(20)	9460(30)	1940(30)	12(5)	1.88

Table S2. Bond lengths (Å) for NaMoO$_3$(IO$_3$)(H$_2$O)

bond	length	bond	length
I(1)-O(3)	1.83(3)	Na(1)-O(1)	2.40(3)
I(1)-O(4)	1.77(2)	Na(1)-O(1)#5	2.30(3)
I(1)-O(5)	1.84(2)	Na(1)-O(3)#5	2.62(3)
I(2)-O(9)	1.70(3)	Na(1)-O(3)	2.37(3)
I(2)-O(10)	1.81(3)	Na(1)-O(6)	2.99(3)
I(2)-O(11)	1.86(2)	Na(1)-O(8)#6	2.85(3)
Mo(1)-O(5)	2.24(2)	Na(1)-O(9)#6	2.68(3)
Mo(1)-O(6)	1.68(3)	Na(2)-O(2)#1	2.36(3)
Mo(1)-O(7)	1.95(2)	Na(2)-O(2)	2.33(3)
Mo(1)-O(7)#1	1.94(2)	Na(2)-O(4)	2.56(3)
Mo(1)-O(8)	1.68(3)	Na(2)-O(10)#7	2.62(3)
Mo(1)-O(9)	2.40(2)	Na(2)-O(10)	2.39(4)
Mo(2)-O(4)#2	2.36(2)	Na(2)-O(13)#6	2.77(3)
Mo(2)-O(11)	2.23(2)	O(1)-H(1A)	0.97
Mo(2)-O(12)	1.68(2)	O(1)-H(1B)	0.97
Mo(2)-O(13)	1.69(2)	O(2)-H(2A)	0.97
Mo(2)-O(14)	1.93(2)	O(2)-H(2B)	0.97

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

Table S3. Band gap and birefringence data for some representative inorganic oxide optical crystals.

	Crystal	Band gap (eV)	Birefringence	Ref.
Alkali metal molybdenum iodate family crystals	$NH_4MoO_3(IO_3)$	3.26	0.083 @1064 nm [cal]	[1]
	γ-$KMoO_3(IO_3)$	3.30	0.087 @1064 nm [cal]	[2]
	$KRb[(MoO_3)_2(IO_3)_2]$	3.32	0.146 @1064 nm [cal]	[1]
	$LiMoO_3(IO_3)$	2.80	0.178 @1064 nm [cal]	[3]
	$Cs_2MoO_2F_3(IO_2F_2)$	3.31	0.204 @1064 nm [cal]	[4]
	$NaMoO_3(IO_3)$	3.19	0.208 @1064 nm [cal]	[2]
	$Rb_2MoO_2F_3(IO_2F_2)$	3.33	0.217 @1064 nm [cal]	[4]
	$AMoO_3(IO_3)$ (A= K, Rb, Cs)	3.10	-	[5]
	δ-$KMoO_3(IO_3)$	3.34	-	[6]
A few commercial crystals	BaB_2O_4		0.122 @532 nm [exp]	[7]
	YVO_4		0.204 @532 nm [exp]	[8]
	$CaCO_3$		0.172 @532 nm [exp]	[9]
A few iodate crystals	ε-$La(IO_3)_3$		0.0295 @visible light [exp]	[10]
	$K_2Zn(IO_3)_3(I_2O_5(OH))(IO_2(OH))(H_2O)$		0.054 @visible light [exp]	[11]
	$Ce(IO_3)_4$		0.052 @546 nm [exp]	[12]
	$CeF_2(IO_3)_2$		0.212 @546nm [exp]	[12]
This work	**$NaMoO_3(IO_3)(H_2O)$**	**3.44**	**0.231 @visible light [exp]**	

Table S4. The calculated dipole moments of anionic groups within a unit cell of $NaMoO_3(IO_3)(H_2O)$.

Polar unit (a unit cell)	Symmetric operation	Dipole moment (D)			
		x	y	z	total
$I(1)O_3$	x, y, z	-2.7502	-8.5311	13.1336	15.9008
$I(1)O_3$	x, 1-y, 0.5+z	-2.7486	8.5315	13.1321	15.8994
$I(2)O_3$	x, 1-y, 0.5+z	-0.0127	9.8102	14.1248	17.1974
$I(2)O_3$	x, y, z	-0.0134	-9.8106	14.1224	17.1956
Net dipole moment (IO_3)		-5.5249	0	54.5129	54.7921
$Mo(1)O_6$	x, 1-y, -0.5+z	-3.6865	-1.0223	-0.9718	3.9471
$Mo(1)O_6$	x, y, z	-3.6878	1.0207	-0.9730	3.9482
$Mo(2)O_6$	x, -1+y, z	4.3588	1.4927	0.9377	4.7017
$Mo(2)O_6$	x, 1-y, 0.5+z	4.3580	-1.4933	0.9390	4.7014
Net dipole moment (MoO_6)		1.3424	0	-0.0681	1.3442
Net dipole moment		-4.1825	0	54.4447	54.6052
Cell volume ($Å^3$)		610.87 (9)			
Dipole moment density		54.6052 /610.87 = 0.0893 D $Å^{-3}$			
Dipole moment density (IO_3)		54.7921 /610.87 = 0.0897 D $Å^{-3}$			

Table S5. Calculated SHG coefficients of $NaMoO_3(IO_3)(H_2O)$.

SHG tensor components	Values (pm/V)	SHG tensor components	Values (pm/V)
d_{111}	-0.24	d_{133}	-0.31
d_{112}	0	d_{222}	0
d_{113}	-0.89	d_{223}	-0.38
d_{122}	-0.32	d_{233}	0
d_{123}	0	d_{333}	-2.29
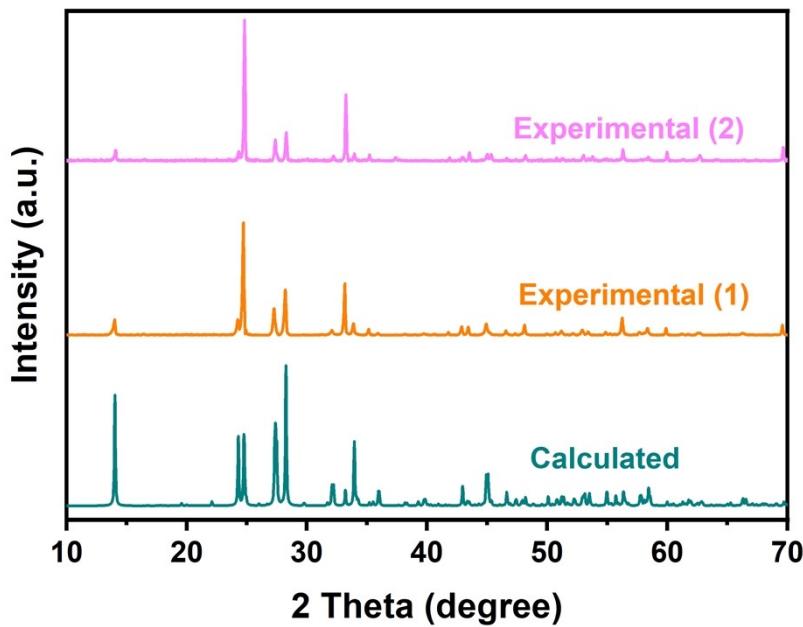
Figure S1. The calculated (Dark Cyan) and experimental (The colors orange and LT Magenta represent fresh samples and samples exposed to humid air for more than 3 months, respectively) powder X-ray diffraction patterns of $NaMoO_3(IO_3)(H_2O)$.


Element	O	Mo	I	Na
Atomic %	69.27	10.53	10.45	9.85
Ratio	7.03	1.06	1.05	1
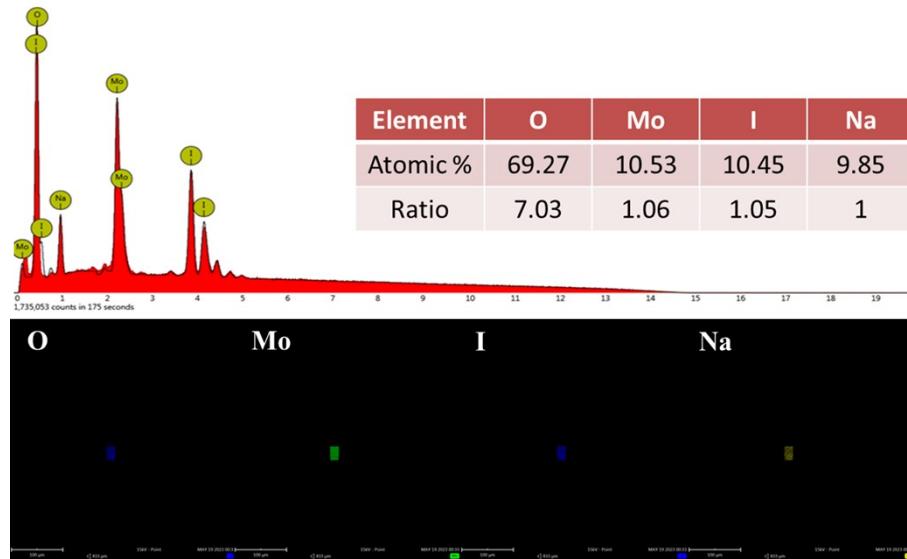
Figure S2. EDS analysis of $NaMoO_3(IO_3)(H_2O)$.
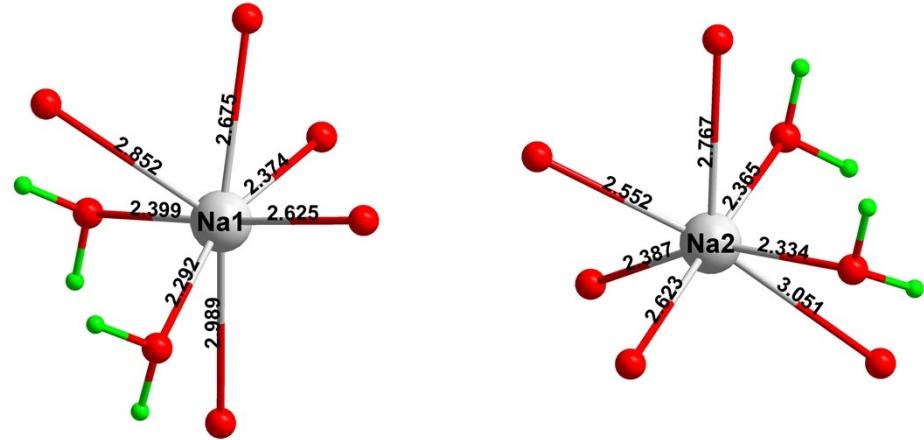
Figure S3. The coordination environment of Na atoms in the structure of $NaMoO_3(IO_3)(H_2O)$
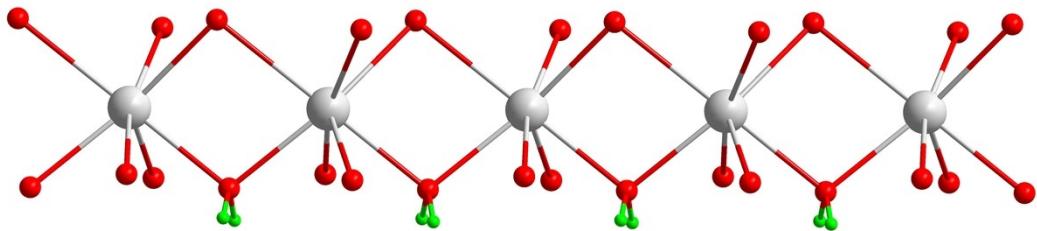

Figure S4. The Na-O line consisted by $[Na(1)O_7]$ polyhedra.
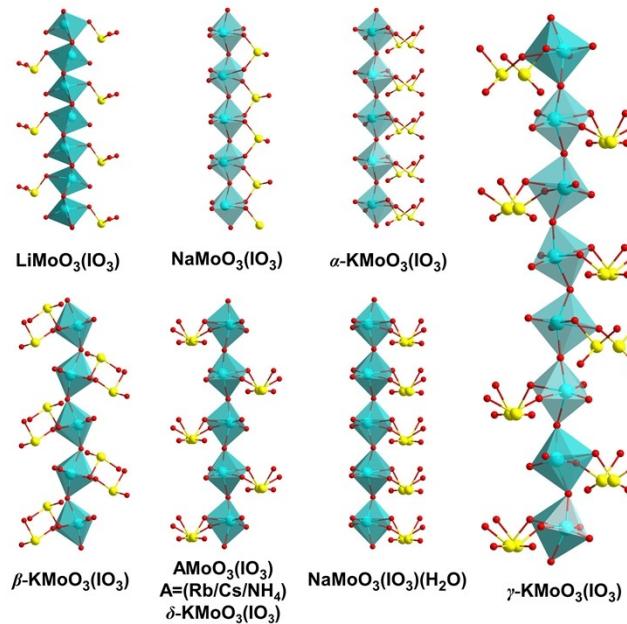
Figure S5. The connection mode of $[MoO_6]$ octahedra and $[IO_3]$ pyramids within the structures of $AMoO_3(IO_3)$ (A = NH_4^+ and alkali-metal ions) family.
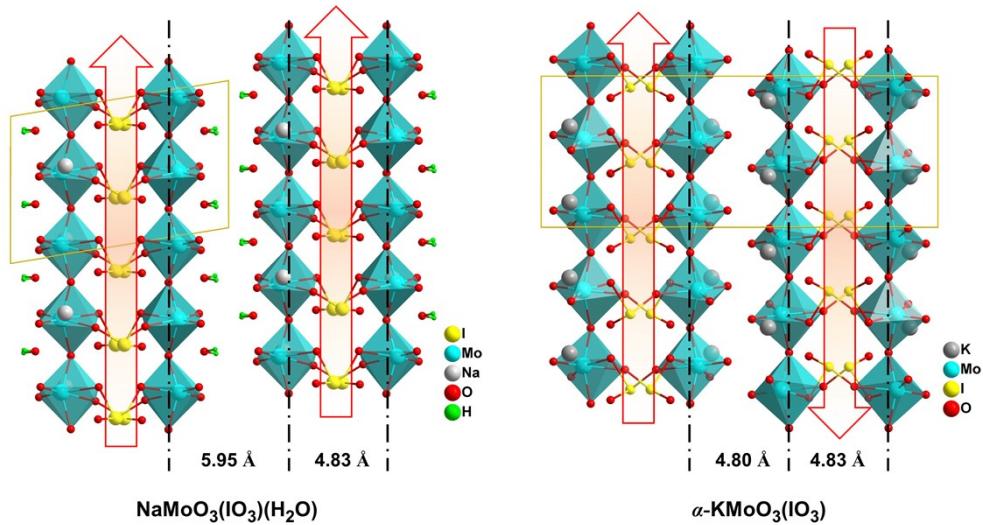
Figure S6. The comparison of layer orientation and distance within the structures of NaMoO$_3$(IO$_3$)(H$_2$O) and α-KMoO$_3$(IO$_3$).
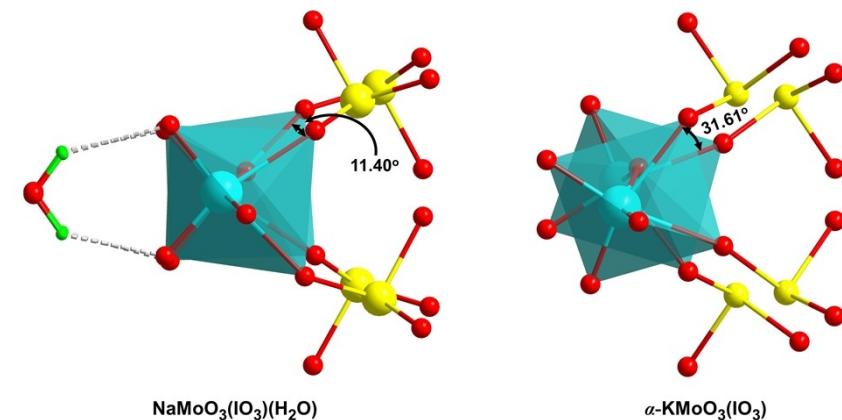

Figure S7. The degree of torsion for adjacent [MoO$_6$] octahedron in Mo-O chain for NaMoO$_3$(IO$_3$)(H$_2$O) and α-KMoO$_3$(IO$_3$).
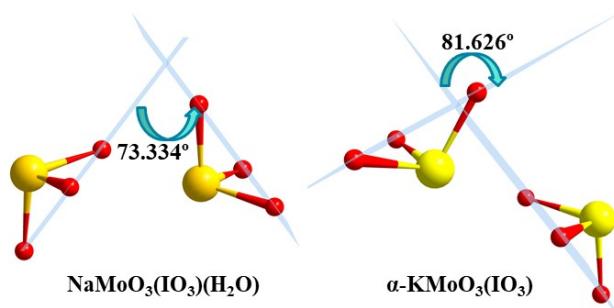
Figure S8. The different dihedral angle between two [IO$_3$] groups in NaMoO$_3$(IO$_3$)(H$_2$O) and α-KMoO$_3$(IO$_3$).
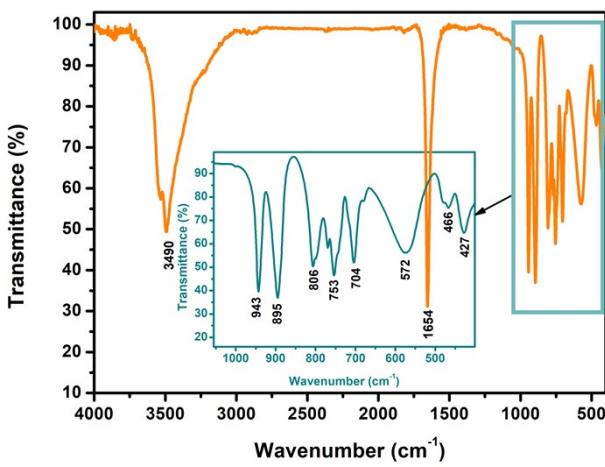
Figure S9. Infrared spectrum of $NaMoO_3(IO_3)(H_2O)$.
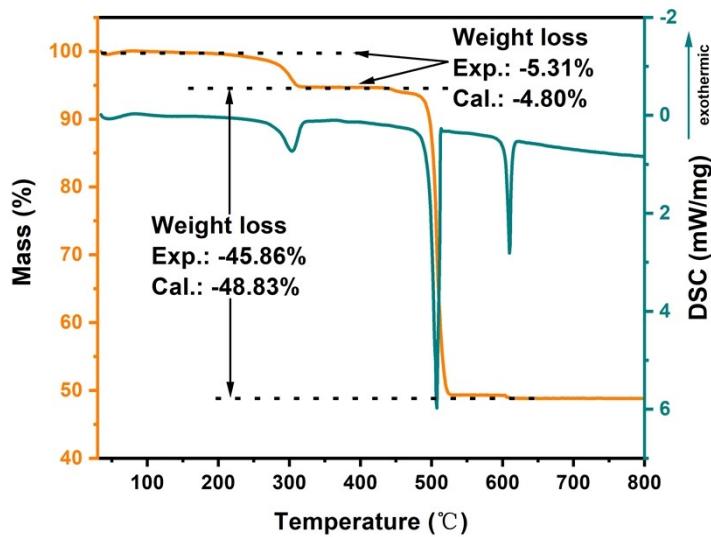

Figure S10. TG and DSC curves of $NaMoO_3(IO_3)(H_2O)$.
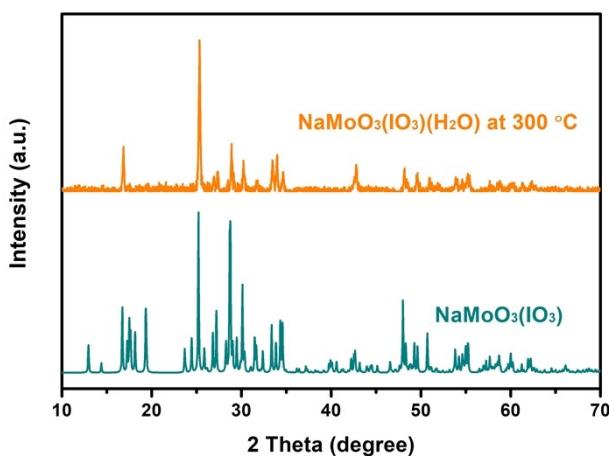
Figure S11. The powder X-ray diffraction patterns of the intermediate after calcination at 300 °C of NaMoO$_3$(IO$_3$)(H$_2$O).
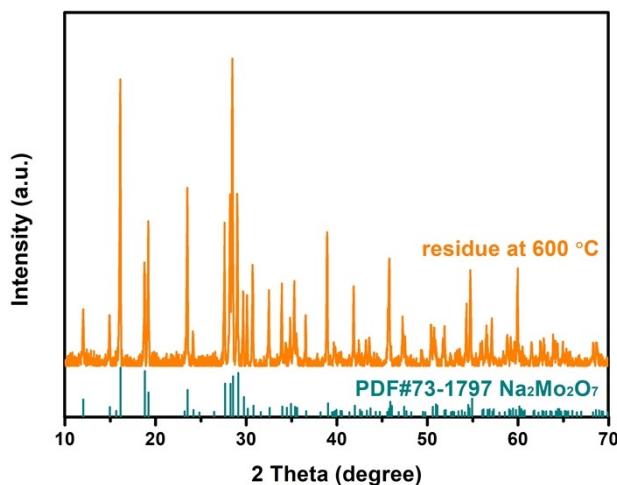

Figure S12. The powder X-ray diffraction patterns of the residue after calcination at 600 °C of NaMoO$_3$(IO$_3$)(H$_2$O).

Notes and references

1   Y. Li, G. Han, H. Yu, H. Li, Z. Yang and S. Pan, Two polar molybdenum(VI) iodates(V) with large second-harmonic generation responses, *Chem. Mater.*, 2019, **31**, 2992-3000.

2   J. Chen, C. Hu, Y. Li, Q. Chen, B. Li and J. Mao, AMoO$_3$(IO$_3$) (A = Na and K): two promising optical materials via properly assembling the Λ-shaped basic building units, *J. Alloys Compd.*, 2022, **894**, 162547.

3   X. Chen, L. Zhang, X. Chang, H. Xue, H. Zang, W. Xiao, X. Song and H. Yan, LiMoO$_3$(IO$_3$): a new molybdenyl iodate based on WO$_3$-type sheets with large SHG response, *J. Alloys Compd.*, 2007, **428**, 54-58.

4   Y. Hu, X. Jiang, C. Wu, Z. Huang, Z. Lin, M. G. Humphrey and C. Zhang, A$_2$MoO$_2$F$_3$(IO$_2$F$_2$) (A= Rb, Cs): strong nonlinear optical responses and enlarged band gaps through fluorine incorporation, *Chem. Mater.*, 2021, **33**,

5700-5708.

5   R. E. Sykora, K. M. Ok, P. S. Halasyamani and T. E. Albrecht-Schmitt, Structural modulation of molybdenyl iodate architectures by alkali metal cations in $AMoO_3(IO_3)$ (A = K, Rb, Cs): a facile route to new polar materials with large SHG responses, *J. Am. Chem. Soc.*, 2002, **124**, 1951-1957.

6   Q. Li, H. N. liu, H. W. Yu, Z. G. Hu, J. Y. Wang, Y. C. Wu, and H. P. Wu, Alignment of Λ-shaped basic building units to construct one new $KMoO_3(IO_3)$ polar polymorph, *Inorg. Chem.*, 2023, **62**, 3896-3903.

7   G. Zhou, J. Xu, X. Chen, H. Zhong, S. Wang, K. Xu, P. Deng, F. Gan, P. Deng and F. Gan, Growth and spectrum of a novel birefringent α-BaB_2O_4 crystal, *J. Cryst. Growth*, 1998, **191**, 517-519.

8   H. T. Luo, T. Tkaczyk, E. L. Dereniak, K. Oka and R. Sampson, High birefringence of the yttrium vanadate crystal in the middle wavelength infrared, *Opt. Lett.*, 2006, **31**, 616-618.

9   G. Ghosh, Dispersion-equation coefficients for the refractive index and birefringence of calcite and quartz crystals, *Opt. Commun.*, 1999, **163**, 95-102.

10 D. Wang, X. Zhang, P. Gong, Z. Lin, Z. Hu and Y. Wu, ε-$La(IO_3)_3$: a polar iodate with high thermal stability and a large second-harmonic-generation response obtained by a supercritical hydrothermal method, *Inorg. Chem.*, 2023, **62**, 6565-6569.

11 J. Chen, P. Yang, H. Yu, Z. Hu, J. Wang, Y. Wu and H. Wu, Designing a strong second-harmonic generation polar iodate by the structure-directing properties of the "Tumbler-like" $[Zn(IO_3)(I_2O_5(OH))]$ polyanions, *ACS Mater. Lett.*, 2023, 1665-1671.

12 T. Wu, X. Jiang, C. Wu, H. Sha, Z. Wang, Z. Lin, Z. Huang, X. Long, M. G. Humphrey and C. Zhang, From $Ce(IO_3)_4$ to $CeF_2(IO_3)_2$: fluorinated homovalent substitution simultaneously enhances SHG response and bandgap for mid-infrared nonlinear optics, *J. Mater. Chem. C*, 2021, **9**, 8987-8993.