Supporting Information

Chromium iodate: the structure and origin of optical second harmonic generation

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Table S1. Crystal data and structure refinement parameters for CIO.

chemical formula	$Cr(IO_3)_3$
Fw	576.70
T (K)	296(2)
crystal system, space group	hexagonal, $P6_3$
Z	2
a (Å)	9.1319(4)
c (Å)	5.2815(3)
V (Å^3)	381.43(4)
D_{calcd} (g/cm^3)	5.021
μ (mm^{-1})	13.666
F(000)	510.0
2θ range (°)	5.15 to 66.59
measd. reflns	4362
indep. reflns/R_{int}	843/0.0486
obs. reflns	843
R_1, wR_2 ($I > 2\sigma(I)$)[a]	0.0326, 0.0653
R_1, wR_2 (all data)[a]	0.0561, 0.0707
GOF on F^2	1.070
Flack parameter	−0.01(6)
$\Delta\rho_{max}/\Delta\rho_{min,}$ e/Å^3	1.81/−1.44

[a]$R_1 = ||F_o| - |F_c||/|F_o|$; $wR_2 = [w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]^{1/2}$.

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (U_{eq}[a], Å$^2 \times 10^3$) for CIO.

Atom	Wyck. site	*x*	*y*	*z*	U_{eq}/Å^2
I(1)	6*c*	3162(1)	3368(1)	4883(4)	15.4(2)
Cr(1)	2*b*	6667	3333	3485(7)	17.5(7)
O(1)	6*c*	4747(10)	2831(10)	5824(15)	17.8(17)
O(2)	6*c*	1669(12)	2187(11)	7300(20)	31(2)
O(3)	6*c*	4227(11)	5477(10)	6387(19)	20.2(17)

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

Table S3. Important bond lengths (Å) for CIO.

Atom	Length/Å	Atom	Length/Å
I(1)–O(1)	1.814(8)	Cr(1)–O(1)	2.001(8)
I(1)–O(2)	1.785(10)	Cr(1)–O(3)^3	1.990(8)
I(1)–O(3)	1.847(9)	Cr(1)–O(3)^4	1.990(8)
Cr(1)–O(1)^1	2.001(8)	Cr(1)–O(3)^5	1.990(8)
Cr(1)–O(1)^2	2.001(8)		

Symmetry transformations used to generate equivalent atoms: ^{1}1+*y*−*x*, 1−*x*, +*z*; ^{2}1−*y*, +*x*−*y*, +*z*; ^{3}+*y*, −*x*+*y*, −1/2+*z*; ^{4}1−*y*+*x*, +*x*, −1/2+*z*; ^{5}1−*x*, 1−*y*, −1/2+*z*.

Table S4. The angle between the lone pair electron direction of I^{5+} ion and the polar axis of $M^{III}(IO_3)_3$ (M^{III} = Cr, Fe, Al, Ga, and In).

Compounds	Shannon ionic radii of M^{III}	Angle (°)
$Cr(IO_3)_3$	0.615	19.90
$Fe(IO_3)_3$	0.645 (high spin)	17.87
$Al(IO_3)_3$	0.535	22.59
$Ga(IO_3)_3$	0.62	22.03
$In(IO_3)_3$	0.80	19.87

Table S5. Metal iodates containing Cr element.

Compound	Space group	SHG efficiency	Ref.
$KCrIO_6$	$P2_1/c$	–	1
$Ca_2(H_2O)(IO_3)_2(CrO_4)$	$P2_1/c$	–	2
$Na_6CaMg(IO_3)_6((Cr_{0.84}S_{0.16})O_4)_2(H_2O)_{12}$	$C2/c$	–	3
$RbUO_2(CrO_4)(IO_3)(H_2O)$	$P\bar{1}$	–	4
$A_2UO_2(CrO_4)(IO_3)_2$ (A = K, Rb, Cs)	$P2_1/c$	–	3
$Th(CrO_4)(IO_3)_2$	$P2_12_12_1$	1 × α-SiO_2 (1064 nm)	5
$Cr(IO_3)_3$	$P6_3$	3.5 × KDP	**this work**

Table S6. Calculated Mulliken bond populations of CIO.

Bond	Population	Length (Å)
I(1)–O(1)	0.27	1.814
I(1)–O(2)	0.42	1.785
I(1)–O(3)	0.19	1.847
Cr(1)–O(1)	0.32	2.001
Cr(1)–O(3)	0.35	1.990

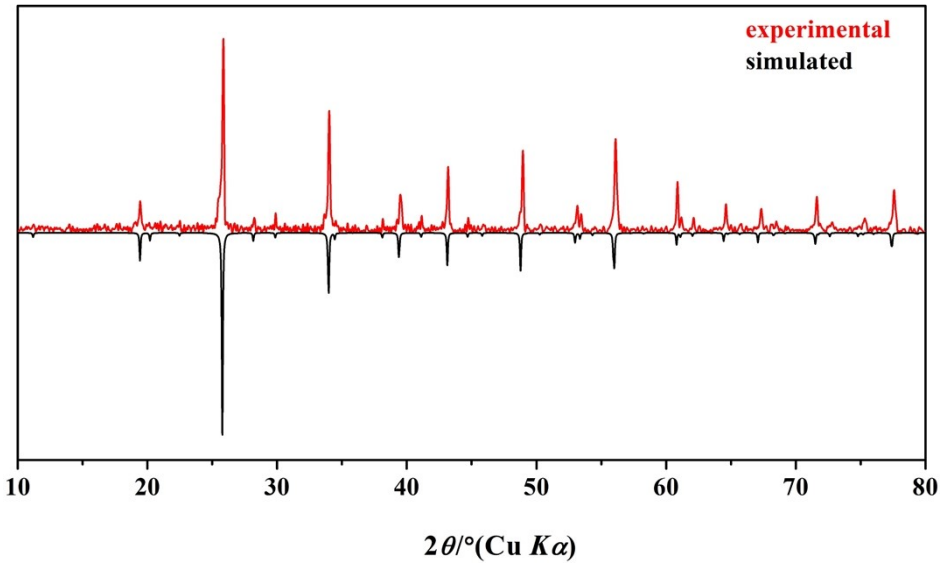


Fig. S1 X-ray powder diffraction pattern of CIO.

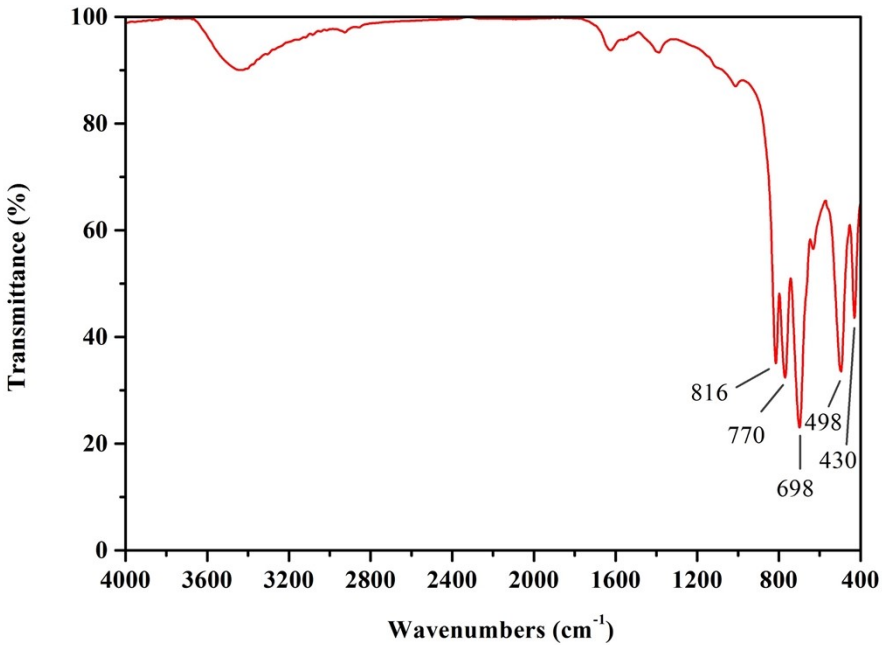


Fig. S2 IR spectrum of CIO.

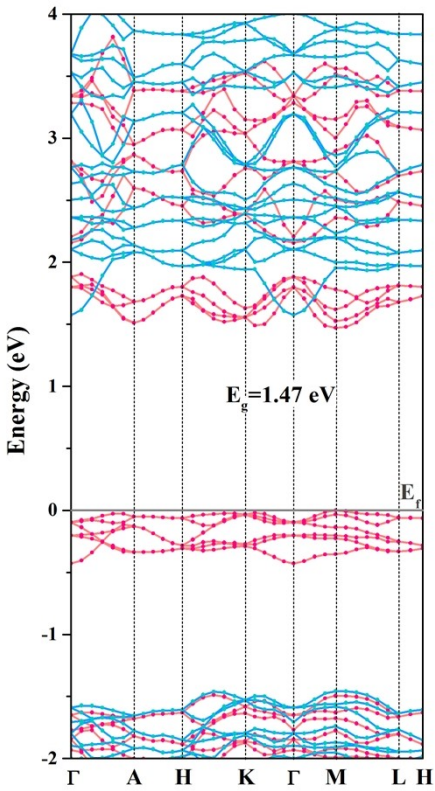


Fig. S3 Calculated band structure for CIO.

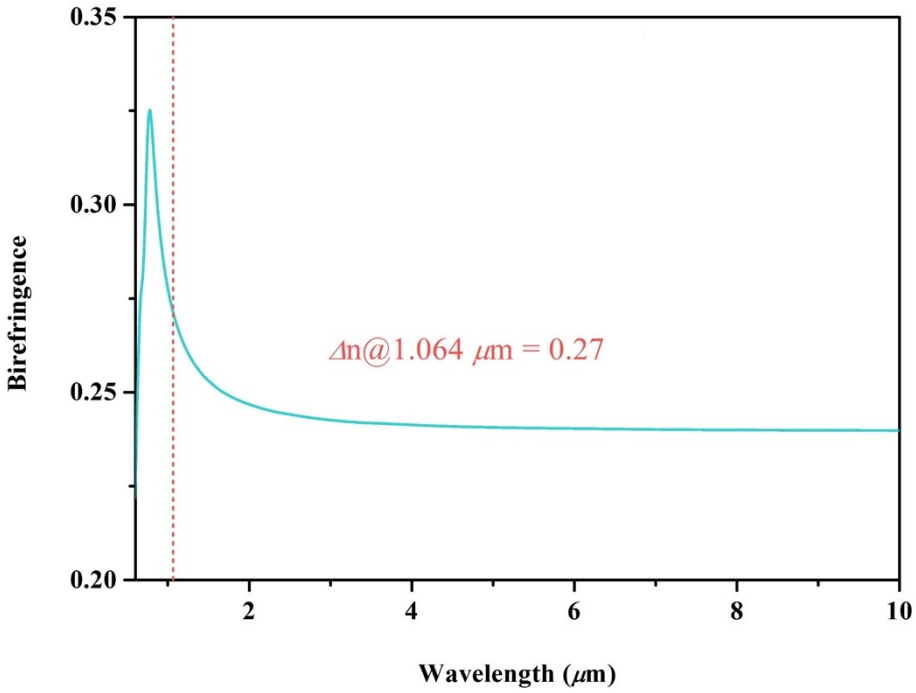
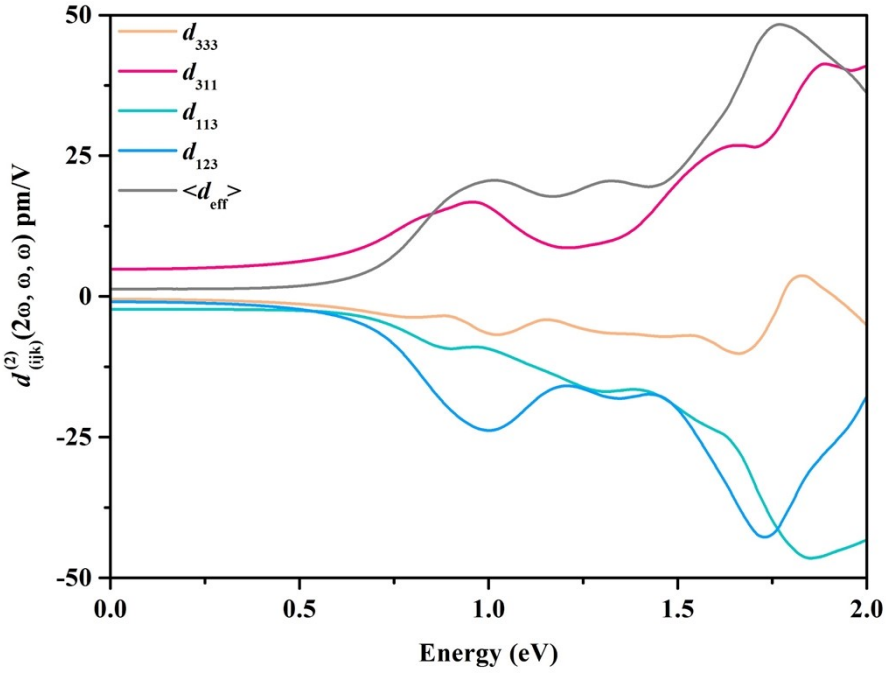
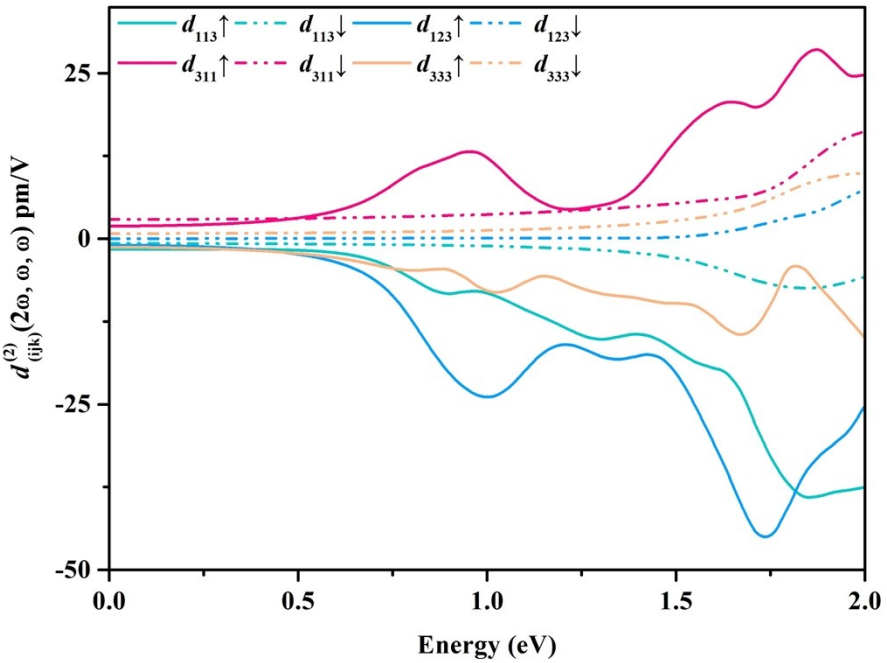


Fig. S4 Calculated birefringence of CIO.



(a)



(b)

Fig. S5 Calculated frequency dependent NLO coefficients in CIO (**a**) and the contribution of spin-up (down) bands (**b**).

References

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