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Supplementary information for

The Second-Harmonic Generation Intensification Derived From Localization conjugated π –orbital in O₂²⁻

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Section S1. Materials and Methods

Synthesis and determination of sample.

All of the chemicals were of analytical grade from commercial sources and used without further purification. K_2CO_3 (99.8%), V_2O_5 (99.0%) and H_2O_2 (30%) were purchased from Adamas. V_2O_5 (0.5g), K_2CO_3 (2.5g) and 1.5ml $H_2O_2(30\%)$ were dissolved in 20 ml distilled water. The solution was transferred to a refrigerator and

vaporized at 5-10°C. After about several weeks, yellow plate-like crystals were obtained (See Figure S1).

Single crystal X-ray diffraction data were collected at room temperature on a Bruker Smart APEX II CCD area detector with graphite-monochromatic Mo K α radiation ($\lambda = 0.71073$ Å). A yellow plate-like crystal was mounted on a glass fiber with epoxy for structure determination. The intensity data sets were corrected with the ω -scan technique. The data were integrated with the CrystalClear program. The intensities were corrected for Lorentz polarization, air absorption, and absorption attributable to the variation in the path length through the detector faceplate. Absorption corrections were also applied based on the Multiscan technique. The structure was solved with direct methods, refined with difference Fourier maps and full-matrix least-squares fitting on F² with SHELXL- 97¹. Moreover, all nonhydrogen atoms were refined with anisotropic thermal parameters. The structure was verified using the ADDSYM algorithm from the program PLATON², and no higher symmetries were found. The details of the crystallographic data and structure refinement information for K₃[V(O₂)₂O]CO₃ are listed in Table S1. Atomic coordinates and isotropic displacement coefficients are listed in Table S1, and bond lengths are listed in Table S2.

Powder X-ray Diffraction.

X-ray diffraction patterns of polycrystalline materials were obtained on a Rigaku Dmax2500 powder X-ray diffractometer by using Cu K α radiation (λ =1.540598 Å) at room temperature in the angular range of 2 θ = 5-75° with a scan step width of 0.05° and a fixed time of 0.2s.

Thermal Analysis.

Thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) were measured on a NETZCH STA 449F3. Reference (Al₂O₃) and crystal samples (3-10 mg) were enclosed in Al₂O₃ crucibles and heated from room temperature to 1100 °C at a rate of 10 °C/min under a constant flow of nitrogen gas.

Diffuse reflectance and transmittance spectroscopy

UV-vis-NIR spectrophotometer of the powder sample was measured at room temperature in the range of 200-2500 nm with BaSO₄ as the standard of 100%

reflectance. The reflectance spectrum was transformed into the absorbance spectrum using the Kubelka–Munk function^{3,4}. The transmittance spectrum was measured from 400 to 600 nm using an unpolished KVCO crystal.

Second-Harmonic Generation.

Polycrystalline second-harmonic generation (SHG) signals were measured using the method source by Kurtz and Perry⁵. Since SHG efficiencies are known to depend strongly on particle size, polycrystalline samples were ground and sieved into the following particle size ranges: 25-45, 45-62, 62-75, 75-109, 109-150, and 150-212 μ m. The samples were pressed between glass microscope cover slides and secured with tape in 1-mm thick aluminum holders containing an 8-mm diameter hole. The samples were then placed in a light-tight box and irradiated with a pulsed laser. The measurements were performed with a Q-switched Nd:YAG laser at 1064nm. A cutoff filter was used to limit background flash-lamp light on the sample, and an interference filter (530±10nm) was used to select the second harmonic for detection with a photomultiplier tube attached to a RIGOL DS1052E 50-MHz oscilloscope.

Computational Descriptions.

First-Principles Calculations.

The first-principles calculations are performed by the psuedopotential⁶ methods implemented in the CASTEP package⁷ based on the density functional theory (DFT).⁸ The optimized norm-conserving pseudopotentials⁹ are used to simulate ion-electron interactions for all constituent elements. A kinetic energy cutoff of 660 eV is chosen with Monkhorst-Pack k-point meshes (3×3×5) spanning less than 0.04/Å³ in the Brillouin zone.¹⁰ The cell parameters and the atomic positions in the unit cell of KVCO are fully fixed. The convergence threshold for SCF tolerance is set as 1.0×10^{-9} eV/atom. Based on the experimental geometry structure, the imaginary part of the dielectric function is calculated and the real part of the dielectric function is determined using the Kramers–Kronig transform,¹¹ and then the refractive indices n and the birefringence Δn are obtained. The shortest SHG output wavelength λ_{PM} is calculated based on the dispersion curves of refractive index (*e.g.*, n_o and n_e), satisfying the condition of n_o $(2\lambda_{PM}) = n_e (\lambda_{PM})$. The second order susceptibility $\chi^{(2)}$ and SHG coefficient $d_{ij} (d_{ij} = 1/2 \chi^{(2)})$ is calculated using an expression originally proposed by Rashkeev *et al*¹² and developed by Lin *et al*:¹³

$$\chi_{ijk} = \chi_{ijk}(VE) + \chi_{ijk}(VH) + \chi_{ijk}(twobands)$$
(1)

where χ_{ijk} (VE), χ_{ijk} (VH) and χ_{ijk} (two bands) denote the contributions from virtualelectron processes, virtual-hole processes and two band processes, respectively. In detail, the formulae for calculating χ_{ijk} (VE), χ_{ijk} (VH) and χ_{ijk} (two bands) are as follows:

$$\chi_{ijk}(VE) = \frac{e^3}{2\hbar^2 m^3} \sum_{vcc'} \int \frac{d^3k}{4\pi^3} P(ijk) Im \left[p_{vc}^{\ i} p_{cc'}^{\ j} p_{c'v}^{\ k} \right] \left(\frac{1}{\omega_{cv}^3 \omega_{vc'}^2} + \frac{2}{\omega_{vc}^4 \omega_{c'v}} \right), \tag{2}$$

$$\chi_{ijk}(VH) = \frac{e^3}{2\hbar^2 m^3} \sum_{vv'c} \int \frac{d^3k}{4\pi^3} P(ijk) Im \left[p_{vv'}^{\ i} p_{v'c}^{\ j} p_{cv}^{\ k} \right] \left(\frac{1}{\omega_{cv}^3 \omega_{v'c}^2} + \frac{2}{\omega_{vc}^4 \omega_{cv'}} \right), \tag{3}$$

$$\chi_{ijk}(twobands) = \frac{e^3}{\hbar^2 m^3} \sum_{vc} \int \frac{d^3k}{4\pi^3} P(ijk) \frac{Im[p_{vc}^{\ i} p_{cv}^{\ j} (p_{vv}^{\ k} - p_{cc}^{\ k})]}{\omega_{vc}^5}$$
(4)

Here, i, j and k are Cartesian components; v and v' denote VB, and c and c' denote CB. P(ijk) denotes full permutation. It is noted that the refractive indices and SHG coefficients can be accurately obtained by DFT in principle because these optical properties are determined by the virtual electronic excited processes, which are described by the first and second order perturbations on the ground state wave functions, respectively.

Furthermore, it should be emphasized that the generalized gradient approximation (GGA) method with PBE functional¹⁴ usually heavily underestimates the energy bandgap E_g . Herein, the scissors-corrected¹⁵ GGA method is employed to calculate the optical properties, where the scissors operator is set as the difference between the experimental and GGA bandgaps. This self-consistent *ab initio* approach has been proven to be an efficient way for the investigation of linear and NLO properties in many types of NLO materials without introducing any experimental parameter.¹⁶ Meanwhile, the linear response method is employed to obtain the phonon dispersion of crystal.¹⁷ The LO-TO phonon frequency splitting at the Γ -point is also included in the phonon calculations. The dispersion separation of 0.01/Å³ is adopted to make sure the good convergence.

In the real-space atom-cutting technique,¹³ the contribution of ion *A* to the *n*th-order susceptibility (denoted as $\chi^{(n)}(A)$) is obtained by cutting all ions except *A* from the original wave functions $\chi^{(n)}(A) = \chi^{(n)}$ (all ions except *A* are cut). In this technique, the "cutting" charge densities are set to be spherical. In fact, this strategy to calculate the respective contribution of ions or groups to the SHG coefficients is not very rigorous, since in the real situation the charge densities around the concerning ions or groups are not spherical. Therefore, as the spherical charge densities are "cut", some charge densities belonging to the concerning ions or groups are very likely to be untouched. It is the repeated calculations of these left charge densities that make the sum of ligand contributions often exceed the total d_{ij} .

The Anionic Group Theory Calculation.

The macroscopic second-order susceptibility $\chi^{(2)}$ could be expressed by Eq. 3 according to the anionic group theory.

$$x_{ijk}^{(2)} = \frac{F}{V} \sum_{p} \sum_{i'jk'} \alpha_{ii'} \alpha_{jj'} \alpha_{kk'} \beta_{i'jk'}^{(2)}(P),$$
(5)

where F is the correction factor of the localized field, V is the volume of the unit cell, $\alpha_{ii'}$,

 $\alpha_{jj'}$, and $\alpha_{kk'}$ are the direction cosines between the macroscopic coordinates axes of the crystal and the microscopic coordinates axes of [CO₃] or [BO₃] groups, and $\beta_{i'j'k'}$ is the microscopic second-order susceptibility tensors of an individual group, which can be calculated with quantum chemistry method.

Because [CO₃] and [BO₃] is a planar group in point group D_{3h}, in the Kleinman approximation, there are only two nonvanishing second-order susceptibility $\beta_{111}^{(2)} = -\beta_{122}^{(2)}$. The geometrical factor, g, could be derived from Eq. (1). and Eq. (2)

could be simplified according to the deduction process⁴⁴:

$$x_{ijk}^{(2)} = \frac{F}{V} \cdot g_{ijk} \cdot \beta_{111}^{(2)}$$
(6)

 $g=\max(g_{ijk}); (i,j,k=1,2,3)$ (7)

In case of unspontaneous polarization, the structural criterion C is defined as:

$$C = \frac{g}{n} \tag{8}$$

where n is the number of anionic groups in a unit cell.

-	
Formula	K ₃ [V(O ₂) ₂ O]CO ₃
Formula Mass (amu)	308.25
Crystal System	Monoclinic
Space Group	Ст
a (Å)	9(2)
b (Å)	9.297
c (Å)	5.601
β (°)	122.89
V(Å ³)	450.0(4)
Z	2
ρ(calcd) (g/cm³)	2.612
Temperature (K)	293(2)
λ(Å)	0.71073
F(000)	300
μ (mm ⁻¹)	2.868
R/wR (I>2σ (I))	0.0223/0.0604
R/wR (all data)	0.0225/0.0605
GOF on F ²	1.146
Absolute Structure Parameter	0.00
$R(F)=\Sigma F_{o} - F_{c} /\Sigma F_{o} $. $wR(F_{o}^{2}) = [\Sigma w(F_{o}^{2} - $	$(F_{c}^{2})^{2}/\Sigma w (F_{o}^{2})^{2}]^{1}$

Table S1. Crystal Data and Structure Refinement for K₃[V(O₂)₂O]CO₃

Table S2.	Atomic	coordinates	and e	quivalent	isotrop	ic dis	olacement	paramet	ers

for K ₃ [V(O ₂) ₂ O]CO ₃					
atom	Х	У	Z	U(eq)	
V(1)	4153(1)	0	2038(1)	12(1)	
K(1)	55(1)	0	2847(2)	21(1)	
K(2)	5520(1)	2184(1)	-1571(1)	21(1)	
O(1)	3083(5)	0	-1407(8)	24(1)	
O(2)	6639(4)	0	2722(8)	17(1)	
O(3)	6616(5)	0	6623(8)	18(1)	
O(4)	9232(5)	0	6960(8)	20(1)	
O(5)	3043(3)	1394(3)	2977(6)	20(1)	
O(6)	4394(3)	2074(3)	2664(7)	22(1)	
C(1)	7554(6)	0	5540(10)	14(1)	

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

V(1)-O(1)	1.623(12)	K(2)-O(6)#9	2.81(6)
V(1)-O(5)#1	1.87(15)	K(2)-O(6)	3.04(17)
V(1)-O(5)	1.87(15)	K(2)-C(1)#10	3.4(3)
V(1)-O(6)	1.950(3)	K(2)-V(1)#9	3.70(5)
V(1)-O(6)#1	1.950(3)	O(1)-K(1)#9	2.9(2)
V(1)-O(2)	2.0(5)	O(1)-K(2)#1	3.0(4)
V(1)-O(3)	2.30(18)	O(2)-C(1)	1.326(7)
V(1)-C(1)	2.6(5)	O(2)-K(2)#1	2.88(2)
V(1)-K(2)#1	3.52(18)	O(2)-K(1)#11	3.0(7)
V(1)-K(2)	3.52(18)	O(3)-C(1)	1.28(17)
V(1)-K(2)#2	3.70(5)	O(3)-K(2)#3	2.68(13)
V(1)-K(2)#3	3.70(5)	O(3)-K(2)#2	2.68(13)
K(1)-O(4)#4	2.77(12)	O(3)-K(1)#12	3.2(3)
K(1)-O(6)#5	2.77(3)	O(4)-C(1)	1.3(3)
K(1)-O(6)#6	2.77(3)	O(4)-K(1)#11	2.77(12)
K(1)-O(1)#2	2.9(2)	O(4)-K(2)#13	2.80(7)
K(1)-O(5)	2.9(5)	O(4)-K(2)#14	2.80(7)
K(1)-O(5)#1	2.9(5)	O(4)-K(1)#12	2.96(6)
K(1)-O(4)#7	2.96(6)	O(5)-O(6)	1.5(2)
K(1)-O(2)#4	3.0(7)	O(5)-K(2)#6	2.66(17)
K(1)-O(3)#7	3.2(3)	O(5)-K(2)#2	2.73(10)
K(1)-C(1)#4	3.3(5)	O(6)-K(1)#15	2.77(3)
K(1)-C(1)#7	3.437(7)	O(6)-K(2)#2	2.81(6)
K(1)-K(2)#5	3.78(4)	O(6)-K(2)#6	3.0(6)
K(2)-O(5)#8	2.66(17)	C(1)-K(1)#11	3.3(5)
K(2)-O(3)#9	2.68(13)	C(1)-K(1)#12	3.437(7)
K(2)-O(5)#9	2.73(10)	C(1)-K(2)#13	3.4(3)
K(2)-O(4)#10	2.80(7)	C(1)-K(2)#14	3.4(3)

Table S3. Bond lengths (Å) for $K_3[V(O_2)_2O]CO_3$

Symmetry transformations used to generate equivalent atoms:

#1 x,-y,z #2 x,y,z+1 #3 x,-y,z+1 #4 x-1,y,z #5 x-1/2,y-1/2,z #6 x-1/2,-y+1/2,z #7 x-1,y,z-1 #8 x+1/2,-y+1/2,z #9 x,y,z-1 #10 x-1/2,y+1/2,z-1 #11 x+1,y,z #12 x+1,y,z+1 #13 x+1/2,-y+1/2,z+1 #14 x+1/2,y-1/2,z+1 #15 x+1/2,y+1/2,z

crystals	SHG Coefficient (visible) (×KDP)	structural criterion C	Densities of the [CO ₃] (n/V) (Å ⁻³)
KVCO	20	1	0.00444
KSrCO ₃ F	3.33	1	0.00889
RbSrCO ₃ F	3.33	1	0.00858
KCaCO ₃ F	3.61	1	0.00998

Table S4. The NLO effects of carbonates with coplannar [CO₃] groups

Table S5 Atom-cutting analysis and calculated SHG coefficients (pm/V) for K₃[V(O₂)₂O](CO₃) and K₃VO₃(CO₃) at 1064 nm

	d_{11}	d_{12}	<i>d</i> ₁₃	d_{15}	d_{24}	<i>d</i> ₃₃
$K_{3}[V(O_{2})_{2}O](CO_{3})$	12.18	-2.33	-1.93	-0.42	6.85	-3.58
Κ	0.22	-0.12	-0.08	-0.01	-0.04	-0.40
CO ₃	5.79	0.55	-0.25	0.27	-0.03	-0.36
$V(O_2)_2O_3$	7.46	-2.61	-0.81	-1.05	6.75	-3.31
O_2	-1.77	-1.08	-0.22	0.41	1.12	1.76
K ₃ VO ₃ (CO ₃)	8.21	-2.30	-2.17	-0.29	4.46	-3.67



Figure S1. The photograph of crystals KVCO



Figure S2. X-ray powder diffraction patterns of K₃[V(O₂)₂O]CO₃. (a) crystal sample and (b) simulation results



Figure S3 TGA and DTA curves of KVCO



Figure S4. (a)Diffuse reflectance and (b) transmittance spectrum of $$K_3[V(O_2)_2O]CO_3$$



Figure S5 The calculated band gap of $K_3[V(O_2)_2O]CO_3$.

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