

## Electronic Supplementary Information

### Three In One: A Cadmium Bismuth Vanadate Nonlinear Optical Crystal Exhibiting a Large Second-Harmonic Generation Response and Enhanced Birefringence

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1. **Table S1.** Selected bond lengths (Å) and angles (deg.) for Cd<sub>2</sub>BiVO<sub>6</sub>.
2. **Table S2.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{Å}^2 \times 10^3$ ) for Cd<sub>2</sub>BiVO<sub>6</sub>.  $U_{eq}$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor, and the bond valence sum for each atom in asymmetric unit.
3. **Fig. S1.** PXRD curves of Cd<sub>2</sub>BiVO<sub>6</sub> after melting compared with the calculated data of Cd<sub>2</sub>BiVO<sub>6</sub>.
4. **Fig. S2.** EDS of Cd<sub>2</sub>BiVO<sub>6</sub> (a) Surface morphology, (b) Atomic ratio of various elements, (c-g) Cd, Bi, V, and O mapping results, respectively.
5. **Fig. S3.** Presentation of Cd<sub>2</sub>BiVO<sub>6</sub> polycrystalline powder.
6. **Fig. S4.** Experimental birefringence measurements. (a-b) Presentation of Cd<sub>2</sub>BiVO<sub>6</sub> before and after extinction under orthotropic polarized light, respectively. (c-d) Observed morphology and theoretical morphology of Cd<sub>2</sub>BiVO<sub>6</sub>, respectively.

**Table S1** Selected bond lengths (Å) and angles (deg.) for Cd<sub>2</sub>BiVO<sub>6</sub>.

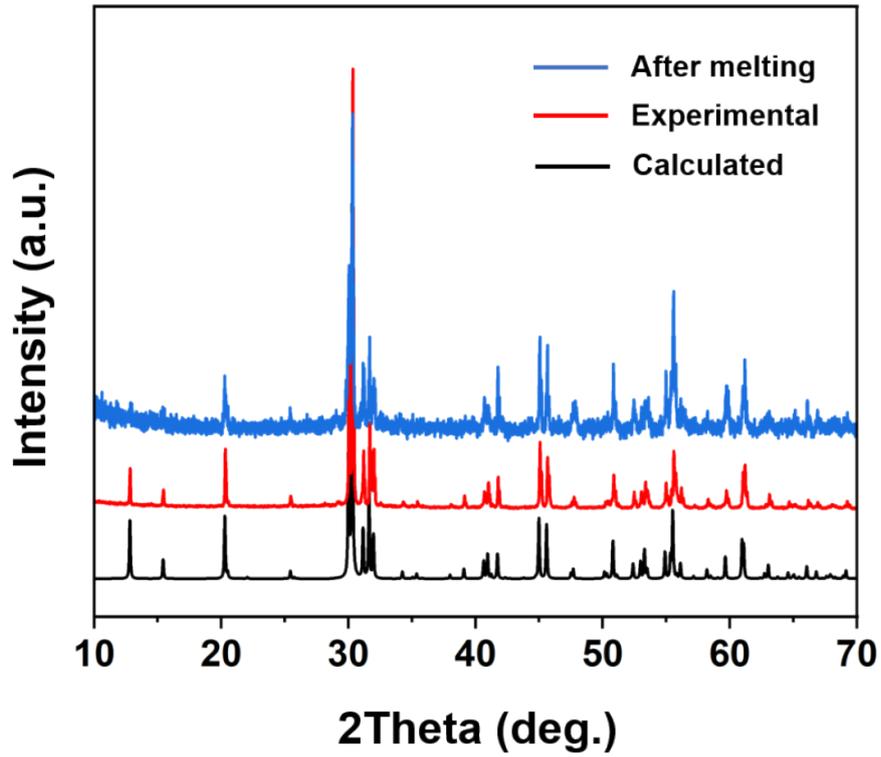
Bi(1)-O(1)#1	2.21(2)	Cd(1)-O(1)	2.241(18)
Bi(1)-O(1)	2.21(2)	Cd(1)-O(1)#6	2.318(18)
Bi(1)-O(1)#2	2.25(2)	Cd(1)-O(2)	2.344(7)
Bi(1)-O(1)#3	2.25(2)	Cd(1)-O(3)#7	2.352(9)
Bi(1)-O(4)#4	2.616(13)	Cd(1)-O(4)#8	2.362(10)
V(1)-O(2)	1.693(11)	Cd(1)-O(3)#3	2.405(10)
V(1)-O(4)	1.739(15)		
V(1)-O(3)	1.740(10)		
V(1)-O(3)#9	1.740(10)		
O(1)#1-Bi(1)-O(1)	74.4(8)	O(1)-Cd(1)-O(1)#6	76.69(13)
O(1)#1-Bi(1)-O(1)#2	78.81(15)	O(1)-Cd(1)-O(2)	90.4(6)
O(1)-Bi(1)-O(1)#2	121.47(11)	O(1)#6-Cd(1)-O(2)	93.1(6)
O(1)#1-Bi(1)-O(1)#3	121.47(11)	O(1)-Cd(1)-O(3)#7	113.4(4)
O(1)-Bi(1)-O(1)#3	78.81(15)	O(1)#6-Cd(1)-O(3)#7	90.9(5)
O(1)#2-Bi(1)-O(1)#3	72.7(8)	O(2)-Cd(1)-O(3)#7	156.2(6)
O(1)#1-Bi(1)-O(4)#4	135.1(4)	O(1)-Cd(1)-O(4)#8	109.3(6)
O(1)-Bi(1)-O(4)#4	135.1(4)	O(1)#6-Cd(1)-O(4)#8	162.1(4)
O(1)#2-Bi(1)-O(4)#4	100.0(5)	O(2)-Cd(1)-O(4)#8	70.4(5)
O(1)#3-Bi(1)-O(4)#4	100.0(5)	O(3)#7-Cd(1)-O(4)#8	101.5(4)
O(2)-V(1)-O(4)	108.2(11)	O(1)-Cd(1)-O(3)#3	80.8(6)
O(2)-V(1)-O(3)	113.7(6)	O(1)#6-Cd(1)-O(3)#3	154.8(5)
O(4)-V(1)-O(3)	56.4(5)	O(2)-Cd(1)-O(3)#3	98.2(7)
O(2)-V(1)-O(3)#9	113.7(6)	O(3)#7-Cd(1)-O(3)#3	87.7(2)
O(4)-V(1)-O(3)#9	56.4(5)	O(4)#8-Cd(1)-O(3)#3	40.3(3)
O(3)-V(1)-O(3)#9	105.7(8)		

Symmetry transformations used to generate equivalent atoms:

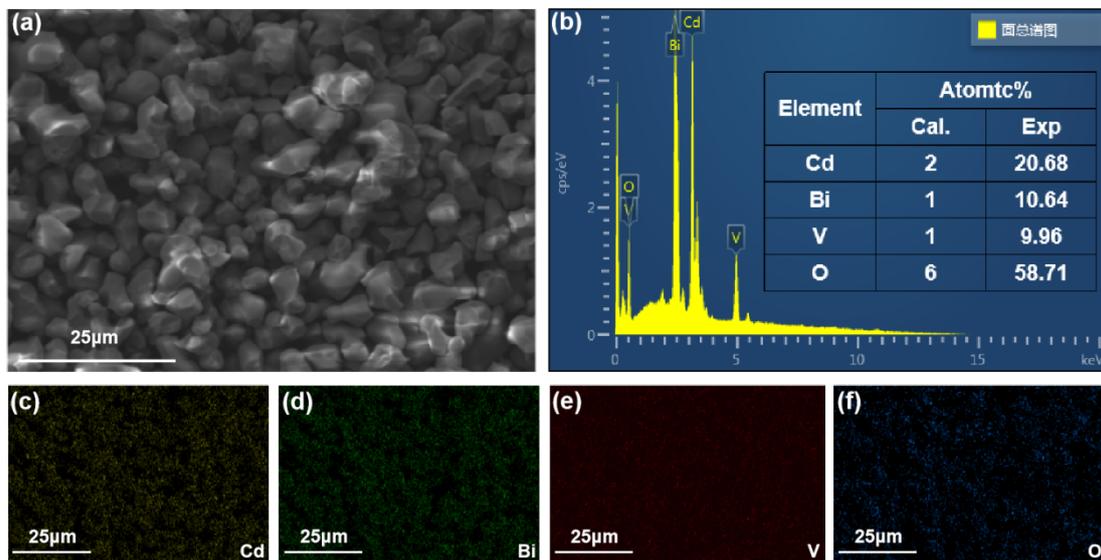
#1 -x,y,z    #2 -x,-y+1,z-1/2    #3 x,-y+1,z-1/2  
#4 x-1/2,y+1/2,z-1    #5 -x,-y+1,z+1/2    #6 x,-y+1,z+1/2  
#7 -x+1/2,y+1/2,z    #8 -x+1,-y+1,z-1/2    #9 -x+1,y,z  
#10 -x+1/2,y-1/2,z    #11 -x+1,-y+1,z+1/2    #12 x+1/2,y-1/2,z+1

**Table S2** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $\text{Cd}_2\text{BiVO}_6$ .  $U_{\text{eq}}$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor, and the bond valence sum for each atom in asymmetric unit.

atom	x	y	z	U(eq)	BVS
Bi(1)	0	5949(1)	2468(2)	9(1)	2.999
Cd(1)	2939(1)	6148(1)	7471(5)	10(1)	1.880
V(1)	5000	3358(2)	7396(18)	7(1)	4.9049
O(1)	1541(7)	5051(15)	4980(50)	9(2)	2.1080
O(2)	5000	4829(9)	7190(60)	9(4)	1.9565
O(3)	3397(11)	2796(8)	8864(19)	16(2)	1.7407
O(4)	5000	2983(11)	10380(30)	16(3)	2.0110



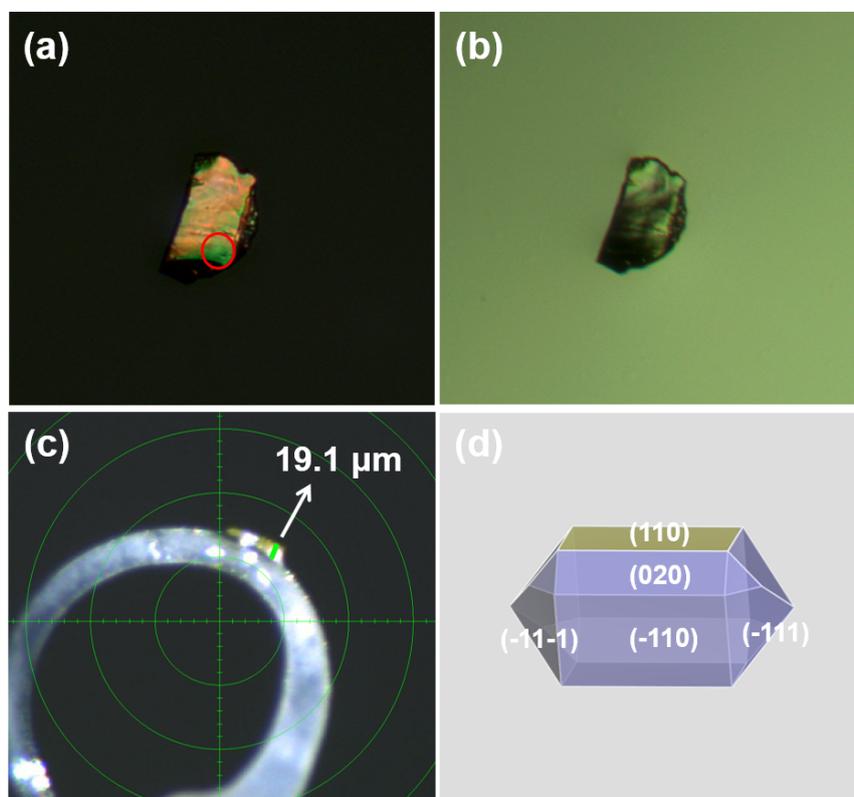
**Fig. S1** PXRD curves of  $\text{Cd}_2\text{BiVO}_6$  after melting compared with the calculated data of  $\text{Cd}_2\text{BiVO}_6$ .



**Fig. S2** EDS of  $\text{Cd}_2\text{BiVO}_6$  (a) Surface morphology, (b) Atomic ratio of various elements, (c-f) Cd, Bi, V, and O mapping results, respectively.



**Fig. S3** Presentation of  $\text{Cd}_2\text{BiVO}_6$  polycrystalline powder.



**Fig. S4** Experimental birefringence measurements. (a-b) Presentation of  $\text{Cd}_2\text{BiVO}_6$  before and after extinction under orthotropic polarized light, respectively. (c-d) Observed morphology and theoretical morphology of  $\text{Cd}_2\text{BiVO}_6$ , respectively.