$Cs_2CdV_2O_6Cl_2$ and $Cs_3CdV_4O_{12}Br$: Two New Non-Centrosymmetric Oxyhalides Containing d^0 and d^{10} Cations and Exhibiting Second Harmonic Generation Activity

Yanjun Li, [*a,b] Dan Zhang, [a] Lili Liu, [b] Weiguo Zhang, [b] Jiang Zhang, [a] Ye Cong, [a] Xuanke Li, [c] P. Shiv Halasyamani [b*]

[a] Department of Chemistry, Key Laboratory of Hubei Province for Coal Conversion and New Carbon Materials, School of Chemistry and Chemical Engineering, Wuhan University of Science and Technology, Wuhan 430081, People's Republic of China

[b] Department of Chemistry, University of Houston, 112 Fleming Building, Houston, Texas 77204, United States

[c] The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan 430081, People's Republic of China

Corresponding Author

*E-mail: yanwatercn@wust.edu.cn, psh@uh.edu.

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Figure S3. Calculated band structure of $Cs_2CdV_2O_6Cl_2$

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Table S1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Cs_2CdV_2O_6Cl_2$.

Atom	*x*	*y*	*z*	U(eq)
$Cs_{(1)}$	6271.3(7)	1292.1(2)	9726.7(7)	25.56(16)
$Cd_{(1)}$	6513.4(18)	5000	5086.8(17)	20.5(2)
$V_{(1)}$	6260(3)	2984.2(5)	4627(3)	15.9(3)
$Cl_{(2)}$	1638(6)	5000	4931(6)	27.0(6)
$Cl_{(1)}$	6427(6)	5000	264(5)	27.0(6)
$O_{(2)}$	6802(13)	3819(3)	5697(13)	31.8(14)
$O_{(1)}$	6248(11)	2988(3)	1603(12)	28.6(13)
$O_{(3)}$	8416(10)	2335(4)	5708(12)	30.6(13)

Table S2. Selected bond lengths and angles for $Cs_2CdV_2O_6Cl_2$.

Bond	Bond Length (Å)	Bond	Bond Length (Å)
$Cd_{(1)} - Cl_{(2)}^{9}$	2.859(4)	$V_{(1)} - O_{(2)}$	1.662(6)
$Cd_{(1)} - Cl_{(2)}$	2.719(4)	$V_{(1)} - O_{(1)}$	1.620(7)
$Cd_{(1)} - Cl_{(1)}^{7}$	2.774(3)	$V_{(1)} - O_{(3)}$	1.785(6)
$Cd_{(1)} - Cl_{(1)}$	2.584(3)	$V_{(1)} - O_{(3)}^{5}$	1.790(6)
$Cd_{(1)} - O_{(2)}^{10}$	2.195(6)	$Cd_{(1)} - O_{(2)}$	2.195(6)
Bond	**Angles(Å)**	**Bond**	**Angles(Å)**
$Cl_{(1)} - Cd_{(1)} - Cl_{(2)}$	87.57(11)	$O_{(2)} - V_{(1)} - O_{(3)}$	112.4(3)
$Cl_{(1)} - Cd_{(1)} - Cl_{(2)}^{13}$	88.99(12)	$O_{(2)} - V_{(1)} - O_{(3)}^{6}$	110.4(3)
$Cl_{(1)} - Cd_{(1)} - Cl_{(1)}^{7}$	177.93(16)	$O_{(1)} - V_{(1)} - O_{(2)}$	109.9(3)
$O_{(2)} - Cd_{(1)} - Cl_{(2)}$	94.40(19)	$O_{(1)} - V_{(1)} - O_{(3)}$	109.0(3)
$O_{(2)}^{14} - Cd_{(1)} - Cl_{(2)}$	94.40(19)	$O_{(1)} - V_{(1)} - O_{(3)}^{6}$	109.1(3)
$O_{(2)}^{14} - Cd_{(1)} - Cl_{(2)}^{13}$	86.11(19)	$O_{(3)} - V_{(1)} - O_{(3)}^{6}$	105.9(2)
$O_{(2)} - Cd_{(1)} - Cl_{(2)}^{13}$	86.11(19)	$Cl_{(2)} - Cd_{(1)} - Cl_{(2)}^{13}$	176.56(15)
$O_{(2)} - Cd_{(1)} - Cl_{(1)}$	98.61(18)	$Cl_{(2)} - Cd_{(1)} - Cl_{(1)}^{7}$	90.36(12)
$O_{(2)}^{14} - Cd_{(1)} - Cl_{(1)}^{7}$	81.54(18)	$Cl_{(1)}^{7} - Cd_{(1)} - Cl_{(2)}^{13}$	93.08(10)
$O_{(2)} - Cd_{(1)} - Cl_{(1)}^{7}$	81.54(18)	$V_{(1)} - O_{(2)} - Cd_{(1)}$	147.6(4)
$O_{(2)}^{14} - Cd_{(1)} - Cl_{(1)}$	98.61(18)	$V_{(1)} - O_{(3)} - V_{(1)}^{5}$	135.2(4)
$O_{(2)} - Cd_{(1)} - O_{(2)}^{14}$	160.9(3)		

Symmetry code: [1]1/2+X,-1/2+Y,+Z; [2]1/2+X,1/2-Y,1+Z; [3]1/2+X,-1/2+Y,1+Z; [4]-1/2+X,-1/2+Y,1+Z; [5]1/2+X,1/2-Y,+Z; [6]-1/2+X,1/2-Y,+Z; [7]+X,+Y,1+Z; [8]-1/2+X,1/2-Y,1+Z; [9]1/2+X,1/2+Y,+Z; [10]1/2+X,1/2+Y,-1+Z; [11]1/2+X,1/2-Y,-1+Z; [12]-1/2+X,1/2+Y,+Z; [13]1+X,+Y,+Z; [14]+X,1-Y,+Z; [15]-1/2+X,1/2-Y,-1+Z; [16]+X,+Y,-1+Z; [17]-1/2+X,1/2+Y,-1+Z; [18]-1+X,+Y,+Z

Table S3. Bond valence sums (BVS) for $Cs_2CdV_2O_6Cl_2$.

Atom	R_0	B	Bong Valence (s_{ij})	Distance (Å)	BVS
Cd					1.97
O1	1.904	0.37	-0.46	2.1950	
O2	1.904	0.37	-0.46	2.1950	
Cl1	2.23	0.37	-0.18	2.8590	
Cl2	2.23	0.37	-0.27	2.7190	
Cl3	2.23	0.37	-0.23	2.7740	
Cl4	2.23	0.37	-0.38	2.5840	
V					5.19
O1	1.803	0.37	-1.46	1.6620	
O2	1.803	0.37	-1.64	1.6200	
O3	1.803	0.37	-1.05	1.7850	
O4	1.803	0.37	-1.04	1.7900	
Cl					1.06
Cd1	2.23	0.37	-0.18	2.8590	
Cd2	2.23	0.37	-0.27	2.7190	
Cd3	2.23	0.37	-0.23	2.7740	
Cd4	2.23	0.37	-0.38	2.5840	
O1					1.95
Cs1	2.417	0.37	-0.10	3.2673	
Cs1	2.417	0.37	-0.11	3.2270	
Cs1	2.417	0.37	-0.10	3.2615	
V1	1.803	0.37	-1.64	1.6199	
O2					2.04
Cs1	2.417	0.37	-0.02	3.7824	
Cs1	2.417	0.37	-0.09	3.2919	
Cd1	1.904	0.37	-0.46	2.1952	
V1	1.803	0.37	-1.46	1.6611	

Table S4. Fractional atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for $Cs_3CdV_4O_{12}Br$.

Atom	*x*	*y*	*z*	U(eq)
$Cs_{(1)}$	10000	7025.6(2)	10010.6(11)	21.25(11)
$Cs_{(2)}$	5000	5000	-170(160)	30(8)
$Cs_{(3)}$	5300(20)	5000	38(14)	37.4(14)
$Cd_{(1)}$	10000	5000	4308.3(13)	15.38(13)
$V_{(1)}$	6918.4(5)	6545.8(3)	4829.7(16)	14.20(13)
$Br_{(1)}$	10000	5000	8955.5(17)	36.7(2)
$O_{(1)}$	5000	6348(2)	3704(7)	23.3(7)
$O_{(2)}$	7500	7500	3864(8)	26.8(8)
$O_{(3)}$	8166(3)	5910.4(15)	3739(5)	26.8(6)
$O_{(4)}$	6905(4)	6515.0(19)	7669(5)	29.5(7)

Table S5. Selected bond lengths and angles for $Cs_3CdV_4O_{12}Br$.

Bond	Bond Length (Å)	Bond	Bond Length (Å)
$Cd_{(1)} - Br_{(1)}{}^{13}$	3.0687(14)	$Cd_{(1)} - O_{(3)}{}^{7}$	2.249(2)
$Cd_{(1)} - Br_{(1)}$	2.6641(13)	$V_{(1)} - O_{(1)}$	1.8057(18)
$Cd_{(1)} - O_{(3)}{}^{15}$	2.249(2)	$V_{(1)} - O_{(2)}$	1.8041(16)
$Cd_{(1)} - O_{(3)}{}^{10}$	2.249(2)	$V_{(1)} - O_{(3)}$	1.656(2)
$Cd_{(1)} - O_{(3)}$	2.249(2)	$V_{(1)} - O_{(4)}$	1.629(3)
Bond	**Angles(°)**	**Bond**	**Angles(°)**
$Br_{(1)} - Cd_{(1)} - Br_{(1)}{}^{14}$	180.0	$O_{(3)} - Cd_{(1)} - O_{(3)}{}^{7}$	89.22(14)
$O_{(3)} - Cd_{(1)} - Br_{(1)}$	98.35(8)	$O_{(3)}{}^{7} - Cd_{(1)} - O_{(3)}{}^{16}$	88.37(14)
$O_{(3)} - Cd_{(1)} - Br_{(1)}{}^{14}$	81.65(8)	$O_{(3)} - Cd_{(1)} - O_{(3)}{}^{10}$	88.37(14)
$O_{(3)}{}^{16} - Cd_{(1)} - Br_{(1)}{}^{14}$	81.65(8)	$O_{(3)}{}^{10} - Cd_{(1)} - O_{(3)}{}^{7}$	163.31(15)
$O_{(3)}{}^{10} - Cd_{(1)} - Br_{(1)}$	98.35(8)	$O_{(3)}{}^{10} - Cd_{(1)} - O_{(3)}{}^{16}$	89.22(14)
$O_{(3)}{}^{7} - Cd_{(1)} - Br_{(1)}{}^{14}$	81.65(8)	$O_{(3)} - V_{(1)} - O_{(1)}$	109.50(15)
$O_{(3)}{}^{7} - Cd_{(1)} - Br_{(1)}$	98.35(8)	$O_{(3)} - V_{(1)} - O_{(2)}$	107.80(13)
$O_{(3)}{}^{16} - Cd_{(1)} - Br_{(1)}$	98.35(8)	$O_{(4)} - V_{(1)} - O_{(1)}$	110.15(17)
$O_{(3)}{}^{10} - Cd_{(1)} - Br_{(1)}{}^{14}$	81.65(8)	$O_{(4)} - V_{(1)} - O_{(2)}$	109.77(19)
$O_{(3)} - Cd_{(1)} - O_{(3)}{}^{16}$	163.31(15)	$O_{(4)} - V_{(1)} - O_{(3)}$	111.14(17)

Symmetry code: [1]2-X,+Y,1+Z; [2]+X,+Y,1+Z; [3]3/2-X,3/2-Y,1+Z; [4]1/2+X,3/2-Y,1+Z; [5]3/2-X,3/2-Y,+Z; [6]1/2+X,3/2-Y,+Z; [7]2-X,+Y,+Z; [8]1-X,1-Y,+Z; [9]1-X,1-Y,-1+Z; [10]+X,1-Y,+Z; [11]1-X,+Y,+Z; [12]+X,1-Y,-1+Z; [13]1-X,+Y,-1+Z; [14]+X,+Y,-1+Z; [15]2-X,1-Y,-1+Z; [16]2-X,1-Y,+Z; [17]3/2-X,3/2-Y,-1+Z; [18]2-X,1-Y,1+Z; [19]1-X,1-Y,1+Z

Table S6. Bond valence sums(BVS) for $Cs_3CdV_4O_{12}Br$.

Atom	R_0	B	Bong Valence (s_{ij})	Distance (Å)	BVS
Cd					2.15
O1	1.904	0.37	-0.39	2.2490	
O2	1.904	0.37	-0.39	2.2490	
O3	1.904	0.37	-0.39	2.2490	
O4	1.904	0.37	-0.39	2.2490	
Br1	2.35	0.37	-0.43	2.6641	
Br2	2.35	0.37	-0.14	3.0687	
V					5.08
O1	1.803	0.37	-1.60	1.6290	
O2	1.803	0.37	-1.49	1.6560	
O3	1.803	0.37	-1.00	1.8040	
O4	1.803	0.37	-0.99	1.8060	
Br					0.57
Cd1	2.35	0.37	-0.43	2.6641	
Cd2	2.35	0.37	-0.14	3.0687	
O1					2.24
Cs1	2.417	0.37	-0.12	3.1907	
Cs2	2.417	0.37	-0.12	3.1907	
V1	1.803	0.37	-1.00	1.8040	
V2	1.803	0.37	-0.99	1.8060	
O2					1.88
Cd1	1.904	0.37	-0.39	2.2490	
V1	1.803	0.37	-1.49	1.6560	

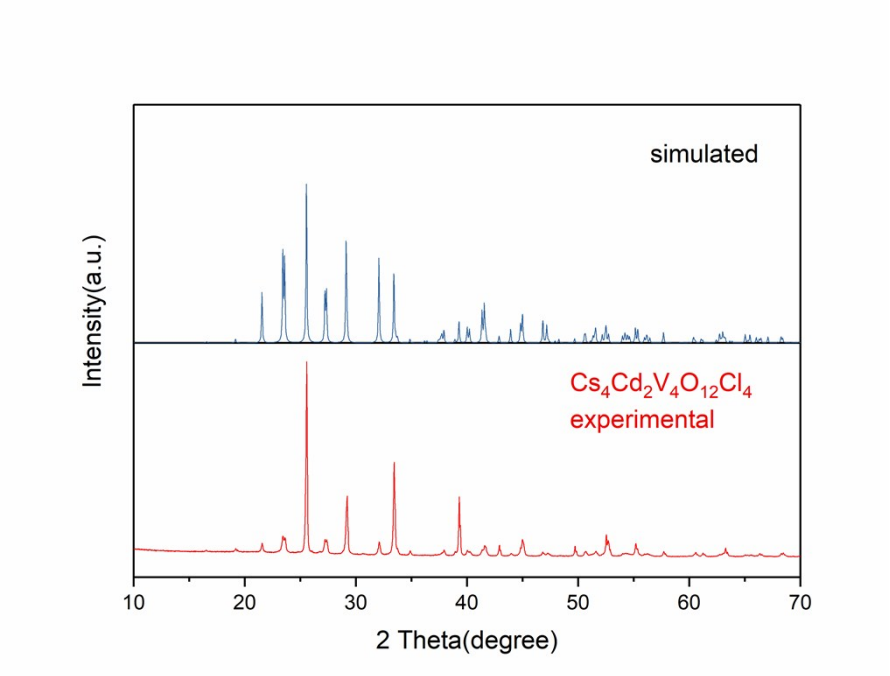

Figure S1. Powder X-ray diffraction patterns of $Cs_2CdV_2O_6Cl_2$. (Red: experimental, and simulated, black)

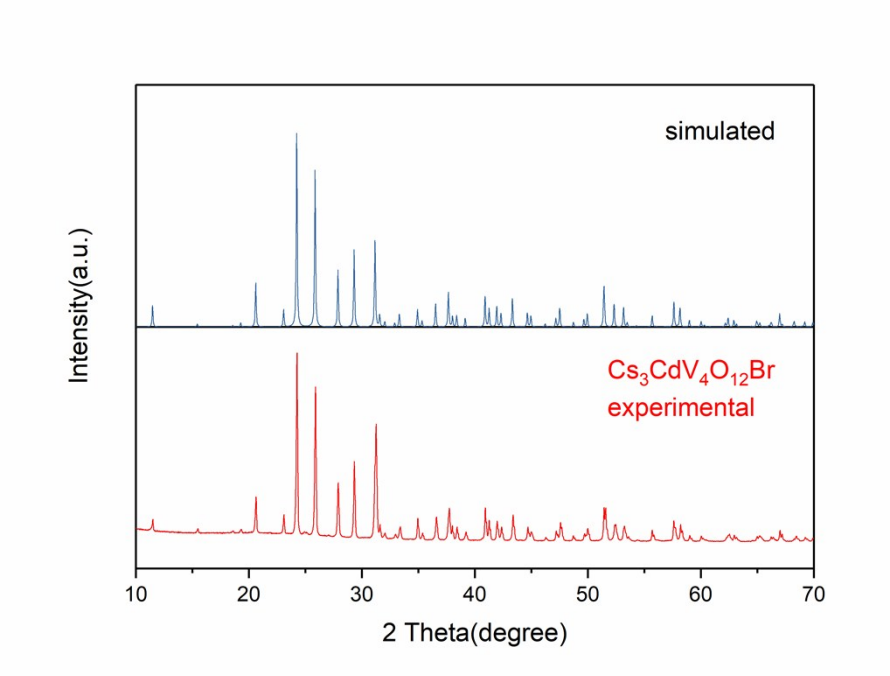

Figure S2. Powder X-ray diffraction patterns of $Cs_3CdV_4O_{12}Br$. (Red: experimental, and simulated, black)

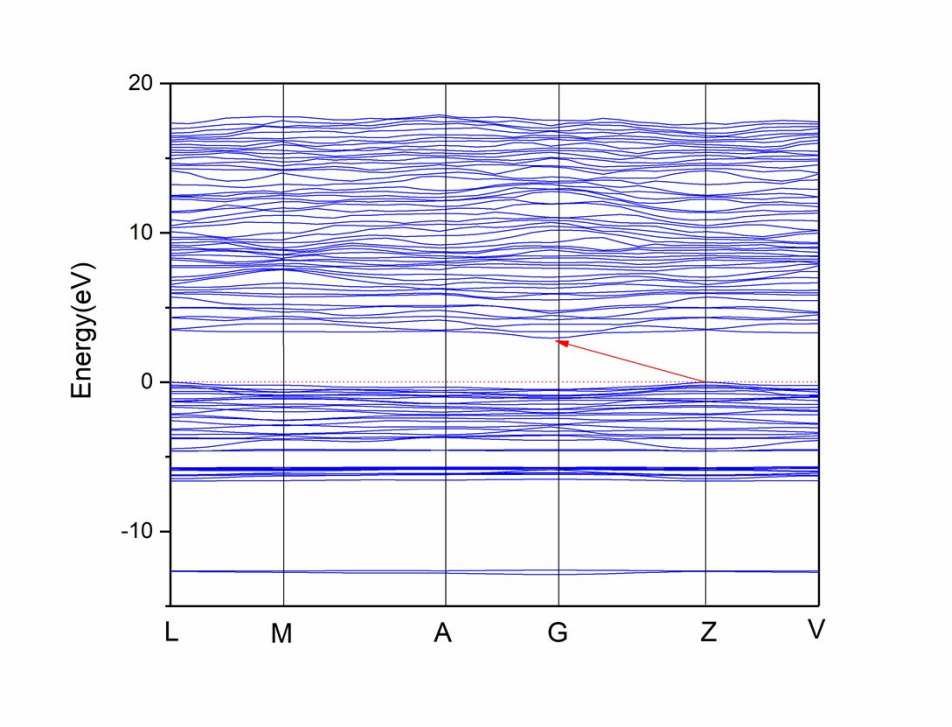

Figure S3. Calculated band structure of $Cs_2CdV_2O_6Cl_2$.

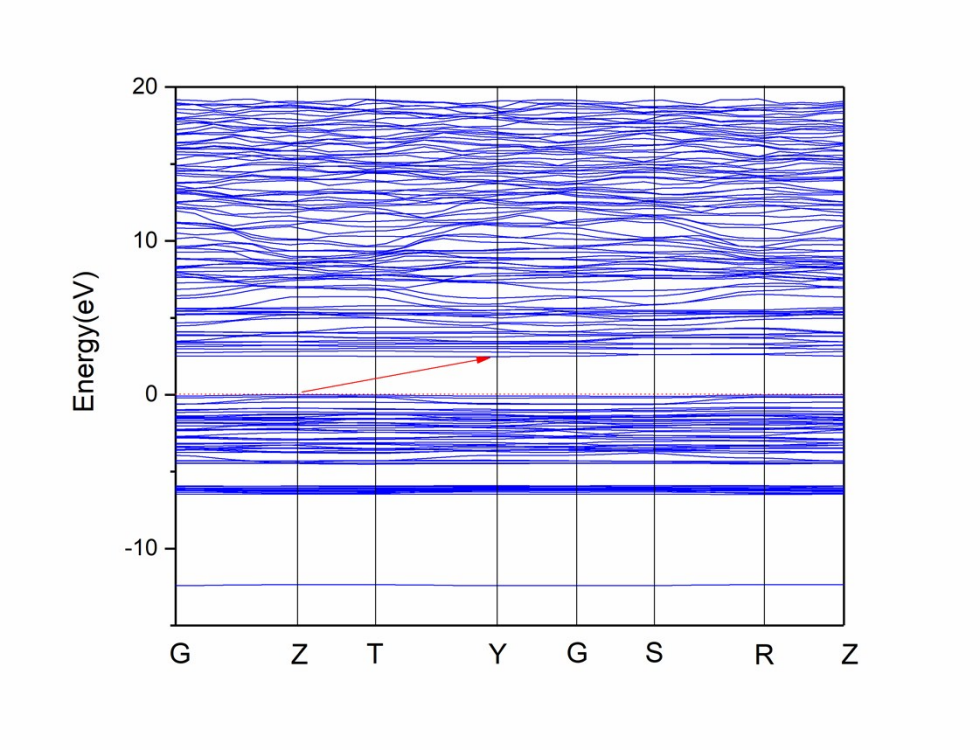

Figure S4. Calculated band structure of $Cs_3CdV_4O_{12}Br$