Electronic Supplementary Information

Two New Tellurite Halides with Cationic Layers: Syntheses, Structures, and Characterizations of $CdPb_2Te_3O_8Cl_2$ and $Cd_{13}Pb_8Te_{14}O_{42}Cl_{14}$

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Table Captions

Table S1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $CdPb_2Te_3O_8Cl_2$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S2. Bond lengths [Å] and angles [°] for $CdPb_2Te_3O_8Cl_2$.

Table S3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Cd_{13}Pb_8Te_{14}O_{42}Cl_{14}$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S4. Bond lengths [Å] and angles [°] for $Cd_{13}Pb_8Te_{14}O_{42}Cl_{14}$.

Table S5. Selected Mulliken atomic populations.

Table S6. Selected bond distances and Mulliken overlap populations for characteristic atomic pairs.

Figure Captions

Figure S1. The EDS spectra of $CdPb_2Te_3O_8Cl_2$ (a) and $Cd_{13}Pb_8Te_{14}O_{42}Cl_{14}$ (b).

Figure S2. (a-g) Coordination of Cd1-Cd7 atoms in $Cd_{13}Pb_8Te_{14}O_{42}Cl_{14}$.

Figure S3. (a-d) Coordination of Pb1-Pb4 atoms in $Cd_{13}Pb_8Te_{14}O_{42}Cl_{14}$.

Figure S4. (a-g) Coordination of Te1-Te7 atoms in $Cd_{13}Pb_8Te_{14}O_{42}Cl_{14}$.

Figure S5. The Cd coordination environments in $C_3H_9Cd_{1.5}Cl_3O_4P$, CdOHCl, $Cd(IO_3)Cl$ and $Cd_5(BO_3)_3Cl$.

Figure S6. The Pb coordination environments in $Pb_3O_2Cl_2$, $Pb_{17}O_8Cl_{18}$, $Ba_{27}Pb_8O_8Cl_{54}$ and $RbPb_8O_4Cl_9$.

Figure S7. XRD patterns of $CdPb_2Te_3O_8Cl_2$ (a) and $Cd_{13}Pb_8Te_{14}O_{42}Cl_{14}$ (b) before and after heating at 550 °C ($CdPb_2Te_3O_8Cl_2$) and 650 °C ($Cd_{13}Pb_8Te_{14}O_{42}Cl_{14}$).

Figure S8. (a) SHG intensities of $CdPb_2Te_3O_8Cl_2$ and $AgGaS_2$ as the references at 2.09 μm radiation. (b) Calculated birefringence (Δn) of $CdPb_2Te_3O_8Cl_2$.

Figure S9. SHG intensities of $CdPb_2Te_3O_8Cl_2$ and KDP as the references at 1064 nm radiation.

Figure S10. The electron density maps of Cd^{2+}, $Pb^{2+}$and Te^{4+}.

Figure S11. Calculated band structures of $CdPb_2Te_3O_8Cl_2$ and $Cd_{13}Pb_8Te_{14}O_{42}Cl_{14}$ under different accuracy.

Table S1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $CdPb_2Te_3O_8Cl_2$.U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)	BVS
Cd(1)	-5000	-5000	-7679(3)	13(1)	1.86
Pb(1)	-3393(1)	-7480(1)	-4664(2)	15(1)	2.27
Te(1)	-6305(1)	-8043(2)	-5051(1)	12(1)	3.83
Te(2)	-5000	-5000	-3486(2)	13(1)	3.91
O(1)	-4347(8)	-5710(20)	-5235(17)	19(4)	2.12
O(2)	-5577(9)	-7290(20)	-3530(20)	20(3)	2.08
O(3)	-5892(11)	-7510(20)	-7157(19)	21(4)	2.08
O(4)	-5902(8)	-10177(19)	-4810(20)	15(3)	2.14
Cl(1)	-2549(4)	-4913(8)	-2346(8)	28(1)	0.75

Table S2. Bond lengths [Å] and angles [°] for $CdPb_2Te_3O_8Cl_2$.

Pb(1)-Cl(1)	3.172(7)	O(1)-Cd(1)-O(2)#5	77.9(5)
Pb(1)-O(1)	2.297(16)	O(1)#3-Cd(1)-O(2)#4	77.9(5)
Pb(1)-O(3)#1	2.363(16)	O(1)#3-Cd(1)-O(2)#5	130.1(6)
Pb(1)-O(4)#2	2.302(16)	O(1)#3-Cd(1)-O(3)#3	89.4(6)
Te(1)-O(2)	1.890(17)	O(1)#3-Cd(1)-O(3)	75.7(6)
Te(1)-O(3)	1.872(16)	O(1)-Cd(1)-O(3)#3	75.7(6)
Te(1)-O(4)	1.896(15)	O(1)-Cd(1)-O(3)	89.4(6)
Te(2)-O(1)	1.909(14)	O(1)-Cd(1)-O(4)#5	104.5(5)
Te(2)-O(1)#3	1.909(14)	O(1)-Cd(1)-O(4)#4	158.1(6)
Te(2)-O(2)#3	2.138(19)	O(1)#3-Cd(1)-O(4)#5	158.1(6)
Te(2)-O(2)	2.138(19)	O(1)#3-Cd(1)-O(4)#4	104.5(5)
Cd(1)-Cd(1)#3	0.000(4)	O(2)#5-Cd(1)-O(2)#4	149.5(8)
Cd(1)-O(1)#3	2.334(14)	O(2)#4-Cd(1)-O(3)#3	67.6(6)
Cd(1)-O(1)	2.334(14)	O(2)#5-Cd(1)-O(3)#3	117.6(6)
Cd(1)-O(2)#4	2.536(19)	O(2)#5-Cd(1)-O(3)	67.6(6)
Cd(1)-O(2)#5	2.536(19)	O(2)#4-Cd(1)-O(3)	117.6(6)
Cd(1)-O(3)#3	2.64(2)	O(3)#3-Cd(1)-O(3)	162.1(7)
Cd(1)-O(3)	2.64(2)	O(4)#4-Cd(1)-O(2)#4	65.0(5)
Cd(1)-O(4)#4	2.350(15)	O(4)#5-Cd(1)-O(2)#5	65.0(5)
Cd(1)-O(4)#5	2.350(15)	O(4)#4-Cd(1)-O(2)#5	92.6(5)
		O(4)#5-Cd(1)-O(2)#4	92.6(5)
O(1)-Pb(1)-Cl(1)	93.6(5)	O(4)#4-Cd(1)-O(3)	68.7(5)
O(1)-Pb(1)-O(3)#1	75.7(6)	O(4)#5-Cd(1)-O(3)	125.9(5)
O(1)-Pb(1)-O(4)#2	95.3(6)	O(4)#5-Cd(1)-O(3)#3	68.7(5)
O(3)#1-Pb(1)-Cl(1)	77.7(5)	O(4)#4-Cd(1)-O(3)#3	125.9(5)
O(4)#2-Pb(1)-Cl(1)	147.6(4)	O(4)#4-Cd(1)-O(4)#5	88.8(8)
O(4)#2-Pb(1)-O(3)#1	74.5(6)	O(3)-Te(1)-O(2)	102.0(8)
O(2)-Te(1)-O(4)	88.0(7)	O(3)-Te(1)-O(4)	98.5(8)
O(1)#3-Te(2)-O(1)	87.5(9)	O(1)#3-Cd(1)-O(1)	68.9(7)
O(1)#3-Te(2)-O(2)	87.2(7)	O(1)-Cd(1)-O(2)#4	130.1(6)
O(1)-Te(2)-O(2)#3	87.2(7)	O(1)-Te(2)-O(2)	91.6(8)
O(1)#3-Te(2)-O(2)#3	91.6(8)	O(2)-Te(2)-O(2)#3	178.3(9)

Symmetry transformations used to generate equivalent atoms:

#1 -x-1,-y-3/2,z+1/2 #2 -x-1,-y-2,z #3 -x-1,-y-1,z

#4 x,y+1/2,z-1/2 #5 -x-1,-y-3/2,z-1/2

Table S3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Cd_{13}Pb_8Te_{14}O_{42}Cl_{14}$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)	BVS
Cd(1)	13010(1)	4958(1)	5437(1)	12(1)	1.95
Cd(2)	7958(1)	5074(1)	405(1)	13(1)	1.93
Cd(3)	-3726(1)	5002(1)	8776(1)	14(1)	2.08
Cd(4)	15410(1)	4995(1)	2843(1)	13(1)	1.96
Cd(5)	11275(1)	5013(1)	3677(1)	13(1)	1.97
Cd(6)	10360(1)	5008(1)	7976(1)	14(1)	1.92
Cd(7)	10000	10000	5000	22(1)	1.89
Pb(1)	913(1)	1895(1)	10872(1)	14(1)	1.97
Pb(2)	8178(1)	1770(1)	3352(1)	16(1)	2.21
Pb(3)	15782(1)	1655(1)	5819(1)	14(1)	2.33
Pb(4)	3598(1)	1900(1)	8323(1)	16(1)	1.99
Te(1)	11903(1)	2709(1)	6680(1)	10(1)	3.84
Te(2)	6922(1)	2514(1)	1692(1)	11(1)	4.12
Te(3)	14272(1)	2745(1)	4218(1)	11(1)	3.92
Te(4)	-427(1)	2438(1)	9194(1)	11(1)	4.04
Te(5)	4748(1)	2291(1)	9988(1)	10(1)	4.06
Te(6)	7454(1)	2290(1)	7343(1)	11(1)	3.89
Te(7)	12107(1)	2302(1)	2582(1)	11(1)	3.90
O(1)	11842(9)	3379(9)	1820(4)	17(2)	2.06
O(2)	11103(9)	4250(9)	6176(4)	18(2)	2.11
O(3)	12388(9)	3677(9)	7446(3)	13(2)	2.10
O(4)	3060(9)	3355(9)	10411(4)	16(2)	2.19
O(5)	7474(10)	3106(9)	2497(4)	20(2)	2.35
O(6)	13843(9)	3169(9)	6293(4)	17(2)	2.28
O(7)	5900(9)	3380(9)	7833(4)	15(2)	2.05
O(8)	4494(10)	3309(9)	9209(4)	22(2)	2.18
O(9)	15950(9)	3644(9)	3755(3)	13(2)	2.18
O(10)	10344(9)	3157(9)	3021(4)	18(2)	2.25
O(11)	8618(9)	3512(9)	1266(3)	13(2)	2.18
O(12)	-91(10)	3390(9)	9969(4)	16(2)	2.19
O(13)	15114(9)	3294(9)	4990(3)	14(2)	2.24
O(14)	-1528(11)	3931(11)	8821(5)	38(3)	2.13
O(15)	13326(9)	3530(9)	3054(4)	18(2)	1.86
O(16)	1381(9)	3242(9)	8787(4)	19(2)	2.04
O(17)	9164(9)	3522(9)	7320(4)	18(2)	1.91
O(18)	6952(9)	3119(9)	6555(3)	17(2)	1.93
O(19)	12789(10)	4240(10)	4396(4)	22(2)	2.16

O(20)	5486(12)	4012(12)	1747(5)	36(2)	2.26
O(21)	6214(12)	3385(11)	10326(7)	56(4)	2.00
Cl(1)	14627(3)	-22(4)	7054(1)	23(1)	0.81
Cl(2)	9448(3)	29(3)	2121(1)	21(1)	0.70
Cl(3)	2038(3)	106(3)	9581(1)	21(1)	0.71
Cl(4)	8887(3)	9970(4)	6190(1)	25(1)	0.88
Cl(5)	6283(3)	-59(4)	8737(1)	29(1)	0.65
Cl(6)	7311(4)	9434(4)	4622(2)	28(1)	0.92
Cl(7)	10925(4)	7066(4)	5156(2)	37(1)	0.62

Table S4. Bond lengths [Å] and angles [°] for $Cd_{13}Pb_8Te_{14}O_{42}Cl_{14}$.

Pb(1)-Cl(3)	3.199(3)	Cd(3)-O(1)#5	2.464(8)
Pb(1)-O(1)#1	2.577(8)	Cd(3)-O(4)#9	2.364(8)
Pb(1)-O(4)	2.433(8)	Cd(3)-O(7)#2	2.492(7)
Pb(1)-O(11)#1	2.541(8)	Cd(3)-O(8)#2	2.318(9)
Pb(1)-O(12)	2.516(8)	Cd(3)-O(14)	2.148(9)
Pb(2)-Cl(2)	3.111(3)	Cd(3)-O(20)#10	2.142(9)
Pb(2)-O(5)	2.265(8)	Cd(4)-O(3)#4	2.316(8)
Pb(2)-O(9)#2	2.640(8)	Cd(4)-O(5)#3	2.522(8)
Pb(2)-O(10)	2.336(8)	Cd(4)-O(6)#4	2.573(8)
Pb(3)-Cl(1)	3.068(3)	Cd(4)-O(7)#6	2.375(8)
Pb(3)-O(6)	2.313(8)	Cd(4)-O(9)	2.324(7)
Pb(3)-O(13)	2.370(8)	Cd(4)-O(15)	2.277(8)
Pb(3)-O(18)#3	2.333(7)	Cd(4)-O(20)#3	2.435(9)
Pb(4)-Cl(5)	3.099(3)	Cd(5)-O(2)#6	2.171(8)
Pb(4)-O(3)#2	2.695(8)	Cd(5)-O(10)	2.359(8)
Pb(4)-O(7)	2.565(8)	Cd(5)-O(15)	2.491(8)
Pb(4)-O(8)	2.429(9)	Cd(5)-O(17)#6	2.505(8)
Pb(4)-O(16)	2.399(8)	Cd(5)-O(18)#6	2.326(8)
Te(1)-Cd(1)	3.3555(10)	Cd(5)-O(19)	2.185(8)
Te(1)-O(2)	1.897(8)	Cd(6)-O(1)#6	2.405(8)
Te(1)-O(3)	1.897(7)	Cd(6)-O(3)	2.322(8)
Te(1)-O(6)	1.864(8)	Cd(6)-O(11)#6	2.311(7)
Te(2)-O(5)	1.859(8)	Cd(6)-O(14)#3	2.502(11)
Te(2)-O(11)	1.896(8)	Cd(6)-O(16)#3	2.522(8)
Te(2)-O(20)	1.828(9)	Cd(6)-O(17)	2.245(8)
Te(3)-Cd(1)	3.3244(10)	Cd(7)-Cl(4)#11	2.570(3)
Te(3)-Cd(1)#4	3.3029(10)	Cd(7)-Cl(4)	2.570(3)
Te(3)-O(9)	1.875(8)	Cd(7)-Cl(6)#11	2.603(3)
Te(3)-O(13)	1.889(7)	Cd(7)-Cl(6)	2.603(3)
Te(3)-O(19)	1.872(8)	Cd(7)-Cl(7)	2.781(3)
Te(4)-Cd(2)#5	3.2953(10)	Cd(7)-Cl(7)#11	2.781(3)
Te(4)-O(12)	1.872(8)	Te(7)-O(10)	1.876(8)
Te(4)-O(14)	1.850(9)	Te(7)-O(15)	1.882(8)
Te(4)-O(16)	1.879(8)	Cd(1)-Cl(7)	2.713(3)
Te(5)-O(4)	1.898(7)	Cd(1)-O(2)	2.260(8)
Te(5)-O(8)	1.884(8)	Cd(1)-O(6)	2.540(8)
Te(5)-O(21)	1.819(10)	Cd(1)-O(9)#4	2.353(7)
Te(6)-Cd(5)#6	3.3544(10)	Cd(1)-O(13)#4	2.402(8)
Te(6)-O(7)	1.889(8)	Cd(1)-O(13)	2.474(8)
Te(6)-O(17)	1.874(8)	Cd(1)-O(19)	2.279(8)
Te(6)-O(18)	1.879(7)	Cd(2)-O(4)#5	2.423(8)
Te(7)-O(1)	1.881(8)	Cd(2)-O(8)#5	2.641(9)

Cd(2)-O(11)	2.375(7)	O(7)#6-Cd(4)-O(6)#4	100.4(3)
Cd(2)-O(12)#7	2.387(8)	O(7)#6-Cd(4)-O(20)#3	69.4(3)
Cd(2)-O(12)#5	2.411(8)	O(9)-Cd(4)-O(5)#3	72.2(3)
Cd(2)-O(16)#5	2.377(9)	O(9)-Cd(4)-O(6)#4	71.9(3)
Cd(2)-O(21)#8	2.188(10)	O(9)-Cd(4)-O(7)#6	159.7(3)
O(16)#5-Cd(2)-O(4)#5	104.3(3)	O(9)-Cd(4)-O(20)#3	125.3(3)
O(16)#5-Cd(2)-O(8)#5	71.3(3)	O(15)-Cd(4)-O(3)#4	174.5(3)
O(16)#5-Cd(2)-O(12)#5	67.7(3)	O(15)-Cd(4)-O(5)#3	101.7(3)
O(16)#5-Cd(2)-O(12)#7	117.4(3)	O(15)-Cd(4)-O(6)#4	119.9(3)
O(21)#8-Cd(2)-O(4)#5	93.1(4)	O(15)-Cd(4)-O(7)#6	93.0(3)
O(21)#8-Cd(2)-O(8)#5	81.5(4)	O(15)-Cd(4)-O(9)	75.8(3)
O(21)#8-Cd(2)-O(11)	81.9(4)	O(15)-Cd(4)-O(20)#3	85.3(3)
O(21)#8-Cd(2)-O(12)#7	90.5(4)	O(20)#3-Cd(4)-O(5)#3	62.1(3)
O(21)#8-Cd(2)-O(12)#5	156.0(4)	O(20)#3-Cd(4)-O(6)#4	153.9(3)
O(21)#8-Cd(2)-O(16)#5	136.3(4)	O(2)#6-Cd(5)-O(10)	85.1(3)
O(1)#5-Cd(3)-O(7)#2	95.2(3)	O(2)#6-Cd(5)-O(15)	149.7(3)
O(4)#9-Cd(3)-O(1)#5	77.4(3)	O(2)#6-Cd(5)-O(17)#6	75.3(3)
O(4)#9-Cd(3)-O(7)#2	172.2(2)	O(2)#6-Cd(5)-O(18)#6	115.3(3)
O(8)#2-Cd(3)-O(1)#5	172.4(3)	O(2)#6-Cd(5)-O(19)	128.8(3)
O(8)#2-Cd(3)-O(4)#9	110.2(3)	O(10)-Cd(5)-O(15)	65.9(3)
O(8)#2-Cd(3)-O(7)#2	77.2(3)	O(10)-Cd(5)-O(17)#6	79.2(3)
O(14)-Cd(3)-O(1)#5	73.9(3)	O(15)-Cd(5)-O(17)#6	90.2(3)
O(11)-Cd(2)-O(8)#5	109.6(3)	O(18)#6-Cd(5)-O(10)	131.6(3)
O(11)-Cd(2)-O(12)#5	110.6(3)	O(18)#6-Cd(5)-O(15)	81.0(3)
O(11)-Cd(2)-O(12)#7	72.7(3)	O(18)#6-Cd(5)-O(17)#6	66.1(3)
O(11)-Cd(2)-O(16)#5	76.1(3)	O(19)-Cd(5)-O(10)	115.7(3)
O(12)#7-Cd(2)-O(4)#5	113.1(3)	O(19)-Cd(5)-O(15)	74.9(3)
O(12)#5-Cd(2)-O(4)#5	76.1(3)	O(19)-Cd(5)-O(17)#6	150.5(3)
O(12)#7-Cd(2)-O(8)#5	171.1(3)	O(19)-Cd(5)-O(18)#6	86.2(3)
O(12)#5-Cd(2)-O(8)#5	111.5(3)	O(1)#6-Cd(6)-O(14)#3	69.1(3)
O(12)#7-Cd(2)-O(12)#5	74.8(3)	O(1)#6-Cd(6)-O(16)#3	125.4(3)
O(1)#1-Pb(1)-Cl(3)	143.81(18)	O(3)-Cd(6)-O(1)#6	161.8(3)
O(4)-Pb(1)-Cl(3)	77.22(18)	O(3)-Cd(6)-O(14)#3	124.0(3)
O(4)-Pb(1)-O(1)#1	74.0(2)	O(3)-Cd(6)-O(16)#3	72.4(3)
O(4)-Pb(1)-O(11)#1	112.1(3)	O(11)#6-Cd(6)-O(1)#6	83.4(3)
O(4)-Pb(1)-O(12)	74.0(3)	O(11)#6-Cd(6)-O(3)	107.0(3)
O(11)#1-Pb(1)-Cl(3)	136.64(17)	O(11)#6-Cd(6)-O(14)#3	91.6(3)
O(11)#1-Pb(1)-O(1)#1	75.7(2)	O(11)#6-Cd(6)-O(16)#3	74.4(3)
O(12)-Pb(1)-Cl(3)	75.24(18)	O(14)#3-Cd(6)-O(16)#3	62.5(3)
O(12)-Pb(1)-O(1)#1	116.3(3)	O(17)-Cd(6)-O(1)#6	93.2(3)
O(12)-Pb(1)-O(11)#1	67.9(2)	O(17)-Cd(6)-O(3)	77.5(3)
O(5)-Pb(2)-Cl(2)	74.0(2)	O(17)-Cd(6)-O(11)#6	173.9(3)
O(5)-Pb(2)-O(9)#2	70.8(3)	O(17)-Cd(6)-O(14)#3	82.5(3)
O(5)-Pb(2)-O(10)	75.7(3)	O(17)-Cd(6)-O(16)#3	103.7(3)

O(9)#2-Pb(2)-Cl(2)	140.79(16)	Cl(4)#11-Cd(7)-Cl(4)	180
O(10)-Pb(2)-Cl(2)	79.1(2)	Cl(4)-Cd(7)-Cl(6)	90.58(9)
O(10)-Pb(2)-O(9)#2	107.8(3)	Cl(4)-Cd(7)-Cl(6)#11	89.42(9)
O(6)-Pb(3)-Cl(1)	76.0(2)	Cl(4)#11-Cd(7)-Cl(6)#11	90.58(9)
O(6)-Pb(3)-O(13)	74.4(3)	Cl(4)#11-Cd(7)-Cl(6)	89.42(9)
O(6)-Pb(3)-O(18)#3	74.7(3)	Cl(4)#11-Cd(7)-Cl(7)#11	88.03(11)
O(13)-Pb(3)-Cl(1)	145.7(2)	Cl(4)-Cd(7)-Cl(7)	88.03(11)
O(18)#3-Pb(3)-Cl(1)	82.59(19)	Cl(4)-Cd(7)-Cl(7)#11	91.97(11)
O(18)#3-Pb(3)-O(13)	105.6(3)	Cl(4)#11-Cd(7)-Cl(7)	91.97(11)
O(3)#2-Pb(4)-Cl(5)	150.09(17)	Cl(6)#11-Cd(7)-Cl(6)	180.00(14)
O(7)-Pb(4)-Cl(5)	79.51(18)	Cl(6)-Cd(7)-Cl(7)	96.67(11)
O(7)-Pb(4)-O(3)#2	76.3(2)	Cl(6)#11-Cd(7)-Cl(7)	83.33(11)
O(8)-Pb(4)-Cl(5)	77.5(2)	Cl(6)#11-Cd(7)-Cl(7)#11	96.67(11)
O(8)-Pb(4)-O(3)#2	111.8(3)	Cl(6)-Cd(7)-Cl(7)#11	83.33(11)
O(8)-Pb(4)-O(7)	73.9(3)	Cl(7)-Cd(7)-Cl(7)#11	180.00(15)
O(16)-Pb(4)-Cl(5)	140.3(2)	O(2)-Cd(1)-O(13)#4	151.9(3)
O(16)-Pb(4)-O(3)#2	68.2(3)	O(2)-Cd(1)-O(19)	116.0(3)
O(16)-Pb(4)-O(7)	118.4(3)	O(6)-Cd(1)-Cl(7)	145.44(19)
O(16)-Pb(4)-O(8)	74.9(3)	O(9)#4-Cd(1)-Cl(7)	95.0(2)
O(3)-Te(1)-O(2)	104.0(3)	O(9)#4-Cd(1)-O(6)	72.1(3)
O(6)-Te(1)-O(2)	87.7(4)	O(9)#4-Cd(1)-O(13)	105.6(3)
O(6)-Te(1)-O(3)	89.3(3)	O(9)#4-Cd(1)-O(13)#4	66.8(3)
O(5)-Te(2)-O(11)	91.2(4)	O(13)-Cd(1)-Cl(7)	145.37(19)
O(20)-Te(2)-O(5)	87.8(4)	O(13)#4-Cd(1)-Cl(7)	85.0(2)
O(20)-Te(2)-O(11)	100.4(4)	O(13)-Cd(1)-O(6)	68.7(2)
O(9)-Te(3)-O(13)	88.1(3)	O(13)#4-Cd(1)-O(6)	116.5(3)
O(19)-Te(3)-O(9)	106.5(4)	O(13)#4-Cd(1)-O(13)	78.3(3)
O(19)-Te(3)-O(13)	87.5(3)	O(19)-Cd(1)-Cl(7)	83.1(2)
O(12)-Te(4)-O(16)	90.6(4)	O(19)-Cd(1)-O(6)	122.2(3)
O(14)-Te(4)-O(12)	98.7(4)	O(19)-Cd(1)-O(9)#4	154.2(3)
O(14)-Te(4)-O(16)	88.6(4)	O(19)-Cd(1)-O(13)#4	87.4(3)
O(8)-Te(5)-O(4)	90.6(4)	O(19)-Cd(1)-O(13)	66.2(3)
O(21)-Te(5)-O(4)	95.4(5)	O(4)#5-Cd(2)-O(8)#5	63.9(2)
O(21)-Te(5)-O(8)	101.7(5)	O(10)-Te(7)-O(15)	89.3(3)
O(17)-Te(6)-O(7)	103.8(3)	O(2)-Cd(1)-Cl(7)	82.9(2)
O(17)-Te(6)-O(18)	89.4(3)	O(2)-Cd(1)-O(6)	65.4(3)
O(18)-Te(6)-O(7)	93.1(3)	O(2)-Cd(1)-O(9)#4	89.1(3)
O(1)-Te(7)-O(15)	104.3(3)	O(2)-Cd(1)-O(13)	124.1(3)
O(10)-Te(7)-O(1)	92.6(3)		

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z+1 #2 x-1,y,z #3 x+1,y,z #4 -x+3,-y+1,-z+1 #11 -x+2,-y+2,-z+1

#5 -x+1,-y+1,-z+1 #6 -x+2,-y+1,-z+1 #7 x+1,y,z-1 #10 -x,-y+1,-z+1

#8 x,y,z-1 #9 -x,-y+1,-z+2

Table S5. Selected Mulliken atomic populations.

Compound				Charge Q (in| e |)	
$CdPb_2Te_3O_8Cl_2$	Atom population	Cd 0.98	Pb 1.06	Te1 1.82	Te2 1.98

Table S6. Selected bond distances and Mulliken overlap populations for characteristic atomic pairs.

Compound-FBB	Value Atomic/ pair	bond distances/ *d* (Å)	overlap populations /(| e |)
$CdPb_2Te_3O_8Cl_2$	Te1-O	1.872-1.896	0.39-0.47
	Te2-O	1.908-2.141	0.23-0.49
	Pb-O	2.299-2.363	0.08-0.11
	Pb-Cl	3.172-3.431	0.00-0.07
	Cd-O	2.334-2.642	0.16-0.18

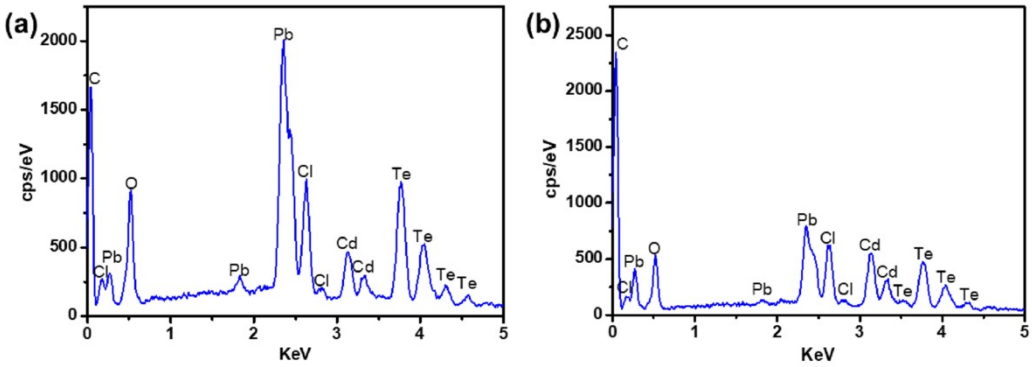

Figure S1. The EDS spectra of $CdPb_2Te_3O_8Cl_2$ (a) and $Cd_{13}Pb_8Te_{14}O_{42}Cl_{14}$ (b).

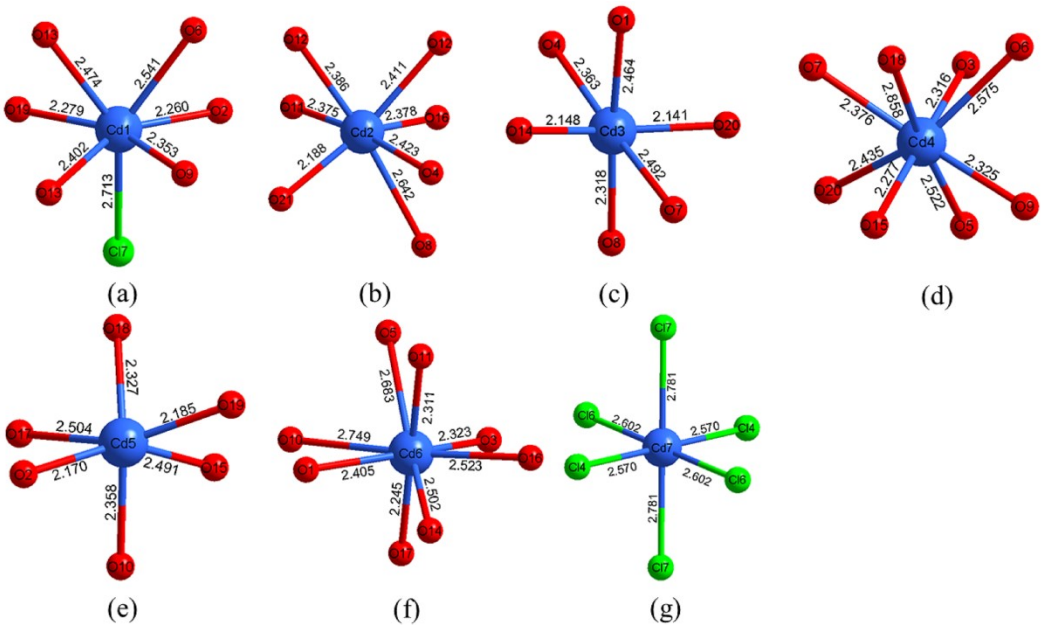

Figure S2. (a-g) Coordination of Cd1-Cd7 atoms in $Cd_{13}Pb_8Te_{14}O_{42}Cl_{14}$.

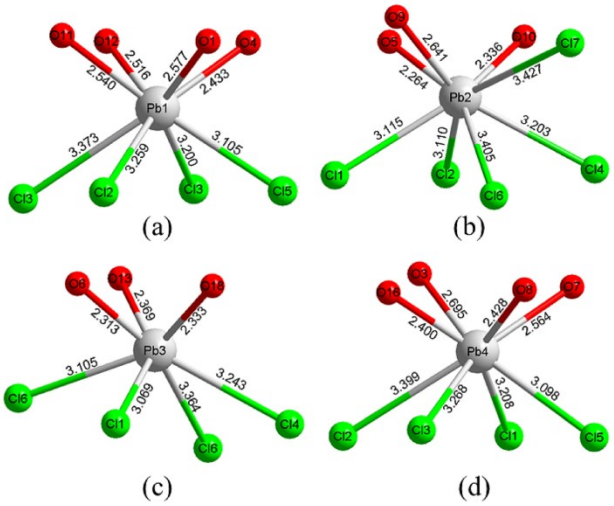

Figure S3. (a-d) Coordination of Pb1-Pb4 atoms in $Cd_{13}Pb_8Te_{14}O_{42}Cl_{14}$.

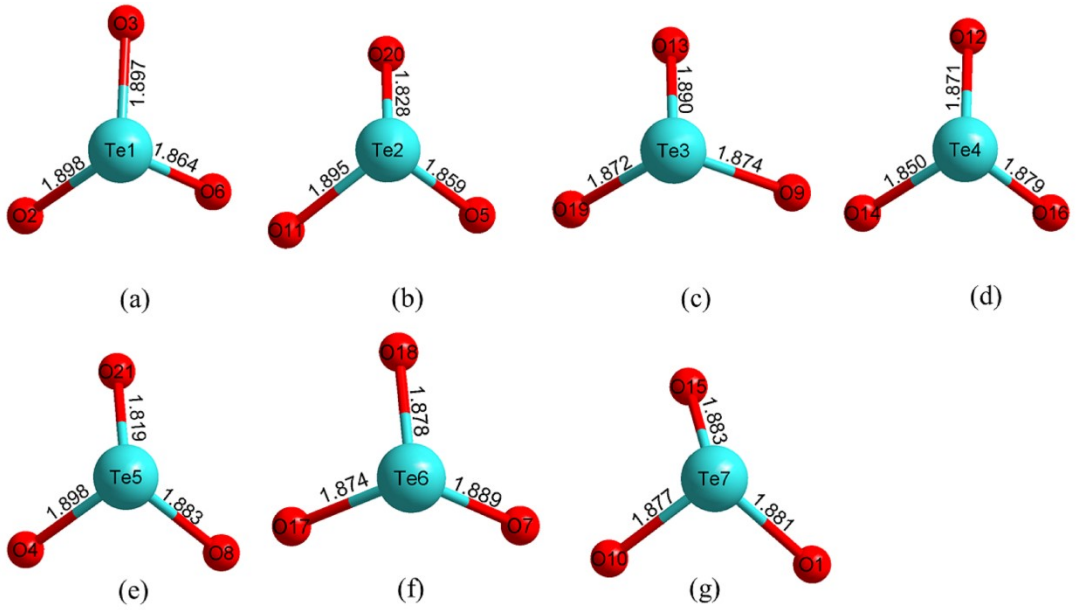

Figure S4. (a-g) Coordination of Te1-Te7 atoms in $Cd_{13}Pb_8Te_{14}O_{42}Cl_{14}$.

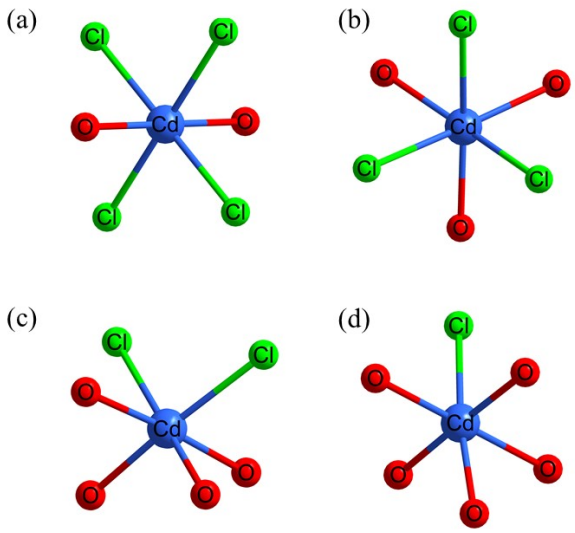

Figure S5. (a) The structure of $[CdO_2Cl_4]$ in $C_3H_9Cd_{1.5}Cl_3O_4P$[1]; (b) The structure of $[CdO_3Cl_3]$ in CdOHCl[2]; (c) The structure of $[CdO_4Cl_2]$ in $Cd(IO_3)Cl$[3]; (d) The structure of $[CdO_5Cl_1]$ in $Cd_5(BO_3)_3Cl$[4].

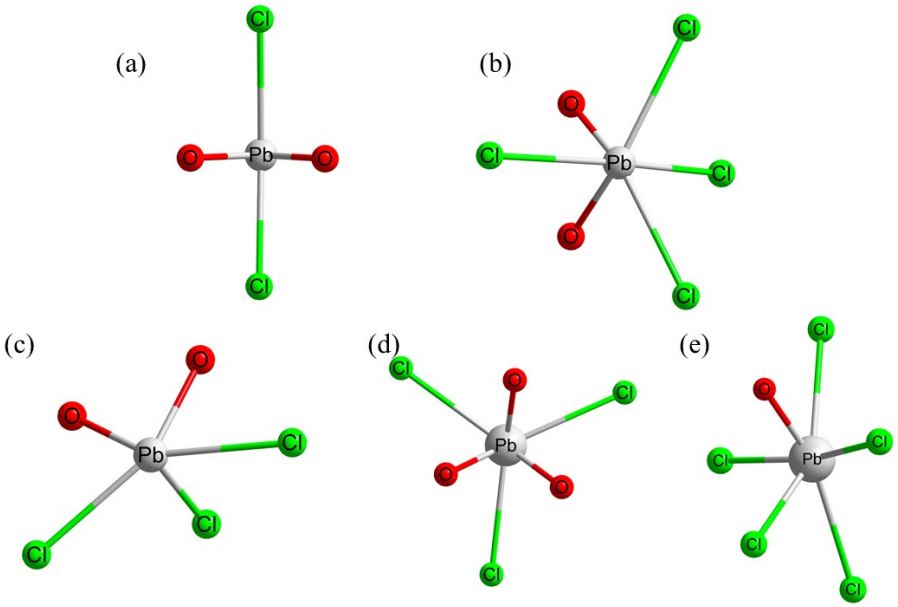

Figure S6. The structure of $[PbO_2Cl_4]$ (a) and $[PbO_2Cl_2]$ (b) in $Pb_3O_2Cl_2$[5]; (c) The structure of $[PbO_2Cl_3]$ in $Pb_{17}O_8Cl_{18}$[6]; (d) The structure of $[PbO_3Cl_3]$ in $Ba_{27}Pb_8O_8Cl_{54}$[7] and $RbPb_8O_4Cl_9$[8]; (e) The structure of $[PbOCl_5]$ in $RbPb_8O_4Cl_9$.

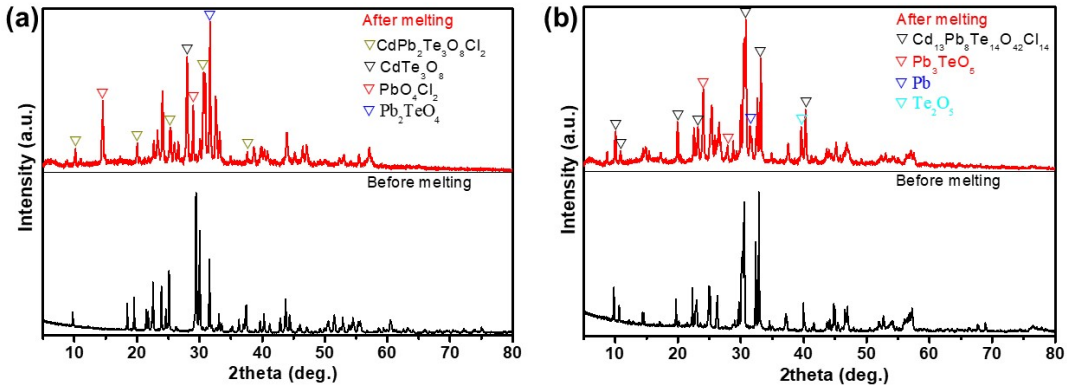

Figure S7. XRD patterns of $CdPb_2Te_3O_8Cl_2$ (a) and $Cd_{13}Pb_8Te_{14}O_{42}Cl_{14}$ (b) before and after heating at 550 °C ($CdPb_2Te_3O_8Cl_2$) and 650 °C ($Cd_{13}Pb_8Te_{14}O_{42}Cl_{14}$).

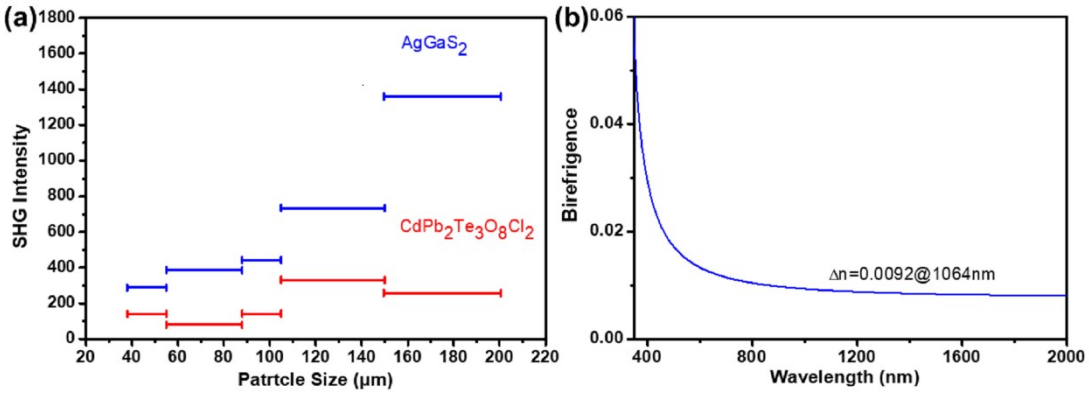

Figure S8. (a) SHG intensities of $CdPb_2Te_3O_8Cl_2$ and $AgGaS_2$ as the references at 2.09 μm radiation. (b) Calculated birefringence (Δn) of $CdPb_2Te_3O_8Cl_2$.

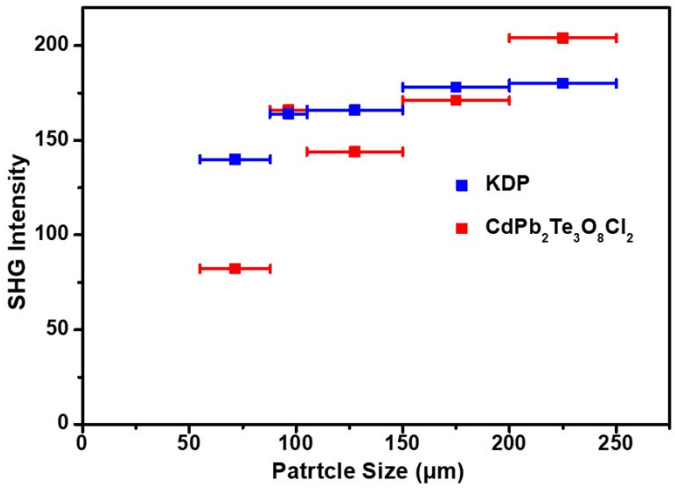

Figure S9. SHG intensities of $CdPb_2Te_3O_8Cl_2$ and KDP as the references at 1064 nm radiation.

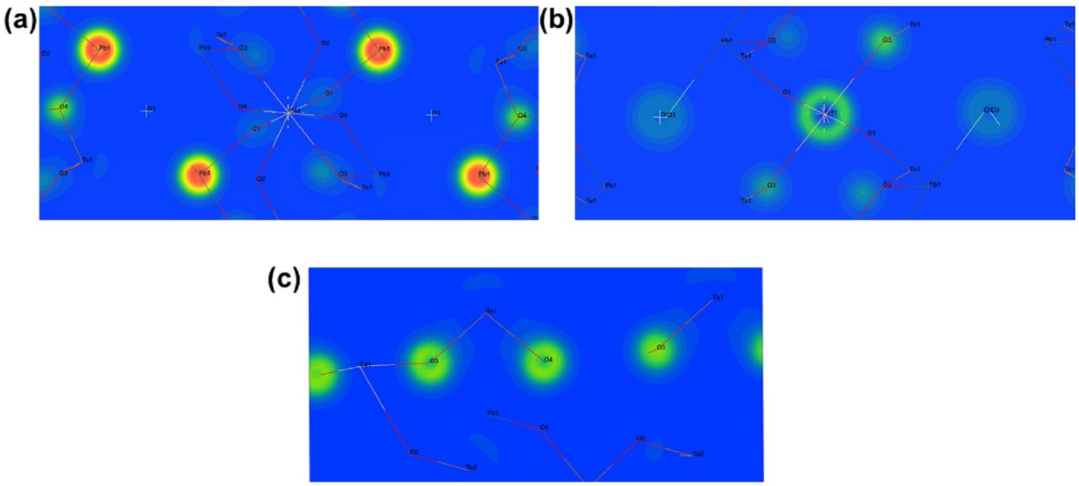

Figure S10. The electron density maps of Cd^{2+}, $Pb^{2+}$and Te^{4+}.

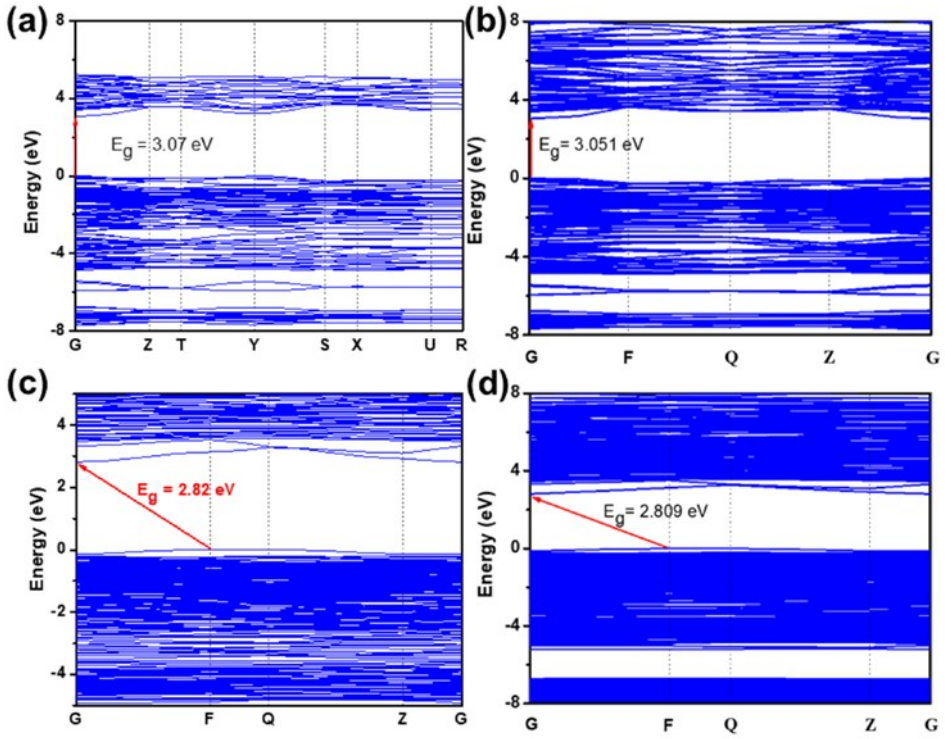

Figure S11. Calculated band structures of $CdPb_2Te_3O_8Cl_2$ and $Cd_{13}Pb_8Te_{14}O_{42}Cl_{14}$ under different accuracy. Band structures of $CdPb_2Te_3O_8Cl_2$ under different accuracy: energy cutoff was set at 910 eV, a spacing of 0.04 $Å^{-1}$ (a) and energy cutoff was set at 700 eV, a spacing of 0.035 $Å^{-1}$ (b); Band structures of $Cd_{13}Pb_8Te_{14}O_{42}Cl_{14}$ under different accuracy: energy cutoff was set at 910 eV, a spacing of 0.04 $Å^{-1}$ (c); energy cutoff was set at 700 eV, a spacing of 0.035 $Å^{-1}$ (d).

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