# Electronic Supplementary Information

## Synthesis, structure and characterizations of $Cd_2TeO_3Cl_2$ with unprecedented $[Cd_2O_6Cl_4]$ octahedral dimers

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## CONTEXT

**Table S1** Atomic coordinates (× $10^4$), equivalent isotropic displacement parameters (Å$^2$ × $10^3$) and bond valence calculations (BVSs) for $Cd_2TeO_3Cl_2$.

| Atom | Wyckoff | x | y | z | U(eq) | BVS |
|---|---|---|---|---|---|---|
| Cd(1) | 2*i* | 7250(1) | 1783(1) | 4616(1) | 14(1) | 1.71 |
| Cd(2) | 2*i* | 2826(1) | 4411(1) | 2670(1) | 14(1) | 1.91 |
| Te(1) | 2*i* | 7729(1) | 7602(1) | 2421(1) | 11(1) | 3.95 |
| O(1) | 2*i* | 9069(3) | 4972(3) | 3535(3) | 16(1) | 2.17 |
| O(2) | 2*i* | 4888(3) | 6641(3) | 2973(3) | 18(1) | 2.07 |
| O(3) | 2*i* | 6658(3) | 8359(3) | 4661(2) | 13(1) | 2.08 |
| Cl(1) | 2*i* | 3049(1) | 6959(1) | -853(1) | 21(1) | 0.77 |
| Cl(2) | 2*i* | 8516(1) | -768(1) | 7539(1) | 18(1) | 0.72 |
| | | GII | | | 0.182 | |

[a] The bond valence sum is calculated by bond-valence theory ($S_{ij}$ = exp[($R_0$-$R$)/$B$, where $R$ is an empirical constant, $R_0$ is the length of bond I (in angstroms), and $B$= 0.37).

[b] The global instability index (GII) calculated using:

$$G = \sqrt{\frac{\sum_{i=1}^{n}(BVS - v_i)}{N}}$$

where N is the number of atoms in the formula unit. The GII is calculated as 0.182 which is lower than 0.2 indicating the rationality of the structure from this side.

**Table S2** Bond lengths [Å] and angles [deg] for $Cd_2TeO_3Cl_2$.

| | | | |
|---|---|---|---|
| Cd(1)-O(1) | 2.2374(17) | O(3)#1-Cd(1)-Cl(2)#2 | 146.56(4) |
| Cd(1)-O(2)#1 | 2.4199(17) | O(3)#4-Cd(1)-O(2)#1 | 125.77(6) |
| Cd(1)-O(3)#1 | 2.3674(16) | O(3)#4-Cd(1)-O(3)#1 | 76.11(6) |
| Cd(1)-O(3)#4 | 2.3063(16) | O(3)#4-Cd(1)-Cl(2) | 79.92(4) |
| Cd(1)-Cl(1)#3 | 2.8816(7) | O(3)#4-Cd(1)-Cl(2)#2 | 77.84(4) |
| Cd(1)-Cl(2) | 2.6528(6) | O(3)#4-Cd(1)-Cl(1)#3 | 80.63(4) |
| Cd(1)-Cl(2)#2 | 2.7893(6) | Cl(2)-Cd(1)-Cl(1)#3 | 154.518(18) |
| Cd(2)-O(1)#6 | 2.2765(16) | Cl(2)-Cd(1)-Cl(2)#2 | 82.66(2) |
| Cd(2)-O(2) | 2.2228(17) | Cl(2)#2-Cd(1)-Cl(1)#3 | 77.270(17) |
| Cd(2)-O(3)#1 | 2.3298(17) | O(1)#6-Cd(2)-O(3)#1 | 105.16(6) |
| Cd(2)-Cl(1) | 2.6450(6) | O(1)#6-Cd(2)-Cl(1) | 86.45(5) |
| Cd(2)-Cl(1)#3 | 2.7369(6) | O(1)#6-Cd(2)-Cl(1)#3 | 158.84(5) |
| Cd(2)-Cl(2)#5 | 2.7174(6) | O(1)#6-Cd(2)-Cl(2)#5 | 80.00(4) |
| Te(1)-O(1) | 1.8801(16) | O(2)-Cd(2)-O(1)#6 | 117.67(6) |
| Te(1)-O(2) | 1.8481(17) | O(2)-Cd(2)-O(3)#1 | 88.59(6) |
| Te(1)-O(3) | 1.8986(16) | O(2)-Cd(2)-Cl(1) | 94.73(5) |
| O(1)-Cd(1)-O(2)#1 | 78.36(6) | O(2)-Cd(2)-Cl(1)#3 | 81.97(5) |
| O(1)-Cd(1)-O(3)#1 | 121.79(6) | O(2)-Cd(2)-Cl(2)#5 | 160.50(5) |
| O(1)-Cd(1)-O(3)#4 | 155.69(6) | O(3)#1-Cd(2)-Cl(1) | 164.78(4) |
| O(1)-Cd(1)-Cl(1)#3 | 87.01(5) | O(3)#1-Cd(2)-Cl(1)#3 | 81.81(4) |
| O(1)-Cd(1)-Cl(2)#2 | 79.06(4) | O(3)#1-Cd(2)-Cl(2)#5 | 78.16(4) |
| O(2)#1-Cd(1)-Cl(1)#3 | 125.50(4) | Cl(1)-Cd(2)-Cl(1)#3 | 83.954(19) |
| O(2)#1-Cd(1)-Cl(2) | 79.55(4) | Cl(1)-Cd(2)-Cl(2)#5 | 94.59(2) |
| O(2)#1-Cd(1)-Cl(2)#2 | 146.59(4) | Cl(2)#5-Cd(2)-Cl(1)#3 | 82.025(19) |
| O(3)#1-Cd(1)-O(2)#1 | 66.85(6) | O(1)-Te(1)-O(3) | 94.69(7) |
| O(3)#1-Cd(1)-Cl(1)#3 | 78.13(4) | O(2)-Te(1)-O(1) | 101.79(8) |
| O(3)#1-Cd(1)-Cl(2) | 112.66(4) | O(2)-Te(1)-O(3) | 89.47(7) |

Symmetry transformations used to generate equivalent atoms:

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

#4 x,y-1,z #5 -x+1,-y,-z+1 #6 x-1,y,z #7 x,y+1,z

#8 x+1,y,z

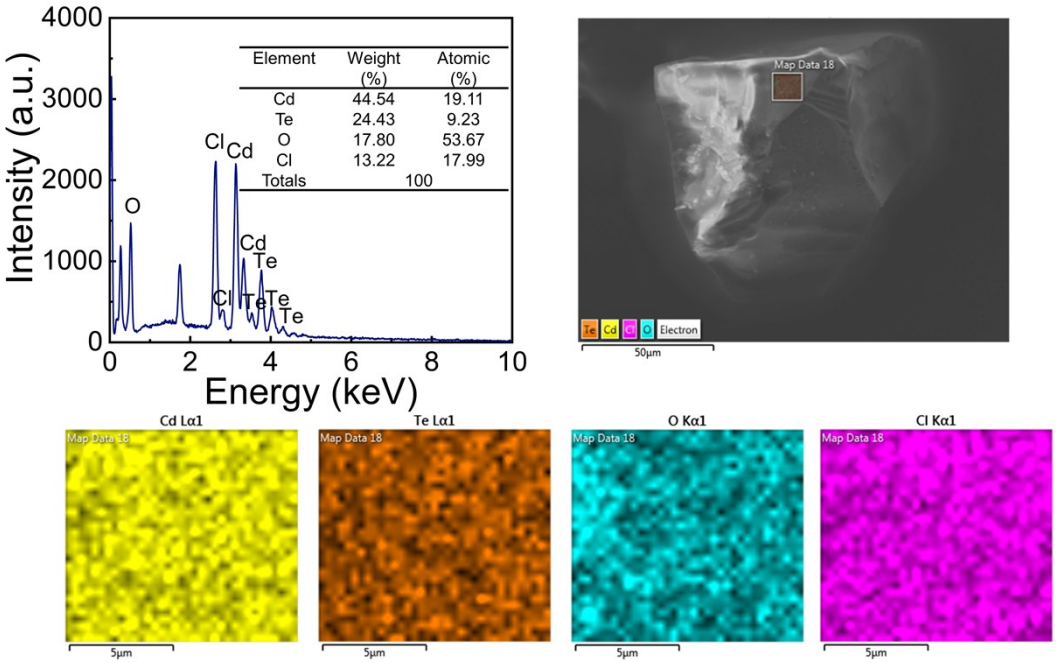


**Fig. S1** The EDS spectrum, SEM image, and EDS mappings of $Cd_2TeO_3Cl_2$.

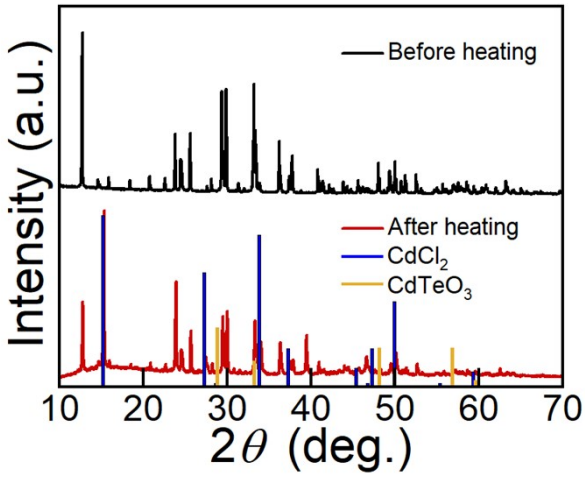


**Fig. S2** The powder XRD patterns of $Cd_2TeO_3Cl_2$ before and after heating experiments, where $CdCl_2$ (PDF #09-0401) and $CdTeO_3$ (PDF #22-0129) XRD patterns used as the references.