

Supporting Information

for

Se-Te Replacement Induced Structural Transition and Enhanced Band Gaps in $\text{Cd}_5\text{Se}_4\text{O}_{12}\text{Cl}_2$ and

$\text{Cd}_5\text{Se}_4\text{O}_{12}\text{Br}_2$

Maqsood Iqbal^{a, b, ‡}, Jiazheng Zhou^{a, ‡}, Aqsa Munawar^{a, b}, Juanjuan Lu^a and Junjie Li^{a, b, *}

^a *Research Center for Crystal Materials; CAS Key Laboratory of Functional Materials and Devices for Special Environments, Xinjiang Key Laboratory of Functional Crystal Materials, Xinjiang Technical Institute of Physics & Chemistry, CAS, Urumqi 830011, China.*

^b *Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China.*

** Corresponding author (E-mail: lijunjie@ms.xjb.ac.cn)*

‡These authors contributed equally.

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Figure Captions

Figure S1. Energy-dispersive X-ray spectroscopy (EDS) analyses for (a) $\text{Cd}_5\text{Se}_4\text{O}_{12}\text{Cl}_2$ and (b) $\text{Cd}_5\text{Se}_4\text{O}_{12}\text{Br}_2$.

Figure S2. Coordination geometries of Cd(1), Cd(2), Cd(3), and Te/Se atoms in $P2_1/c$ - $\text{Cd}_5\text{Te}_4\text{O}_{12}\text{X}_2$, ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) (a) and $C2/c$ - $\text{Cd}_5\text{Se}_4\text{O}_{12}\text{X}_2$, ($\text{X} = \text{Cl}, \text{Br}$) (b).

Figure S3. Pseudo-ternary diagram of the CdO – SeO_2 – CdX_2 ($\text{X} = \text{Cl}/\text{Br}$) system.

Figure S4. Experimental and Rietveld refinement XRD patterns of $\text{Cd}_5\text{Se}_4\text{O}_{12}\text{Br}_2$.

Table S1. Selected bond lengths [\AA] for $\text{Cd}_5\text{Se}_4\text{O}_{12}\text{Cl}_2$.

Atom	Atom	Length/ \AA	Atom	Atom	Length/ \AA
Cd1	O2 ¹	2.514(3)	Cd3	Cl1 ¹⁰	2.625(2)
Cd1	O2 ²	2.514(3)	Cd3	Cl2	2.591(2)
Cd1	O3 ³	2.323(3)	Cd3	Cl2 ¹⁰	2.594(2)
Cd1	O3	2.323(3)	Cd3	O1	2.234(3)
Cd1	O4 ¹	2.480(3)	Cd3	O2	2.235(3)
Cd1	O4 ²	2.480(3)	Cd3	O5 ¹¹	2.477(3)
Cd1	O5 ⁴	2.376(3)	Cd3	O6 ¹²	2.415(3)
Cd1	O5 ⁵	2.376(3)	Se1	O2	1.731(3)
Cd2	O1 ⁶	2.283(3)	Se1	O4	1.667(3)
Cd2	O2 ⁷	2.326(3)	Se1	O5	1.691(3)
Cd2	O3 ⁸	2.290(3)	Se2	O1	1.714(3)
Cd2	O4	2.291(3)	Se2	O3	1.683(3)
Cd2	O6 ⁹	2.253(3)	Se2	O6	1.690(3)
Cd3	Cl1	2.582(2)			

¹1-X,1-Y,1-Z; ²+X,1-Y,1/2+Z; ³1-X,+Y,3/2-Z; ⁴1-X,-Y,1-Z; ⁵+X,-Y,1/2+Z; ⁶1-X,-1+Y,1/2-Z; ⁷1-X,+Y,1/2-Z; ⁸+X,-Y,-1/2+Z; ⁹+X,1-Y,-1/2+Z; ¹⁰3/2-X,1/2-Y,1-Z; ¹¹+X,1+Y,+Z; ¹²+X,-1+Y,+Z;

Table S2. Selected bond lengths [\AA] for $\text{Cd}_5\text{Se}_4\text{O}_{12}\text{Br}_2$.

Atom	Atom	Length/ \AA	Atom	Atom	Length/ \AA
Cd1	O1 ¹	2.466(4)	Cd3	Br1	2.7849(13)
Cd1	O1 ²	2.466(4)	Cd3	Br2	2.7135(16)
Cd1	O4 ³	2.379(4)	Cd3	Br2 ¹⁰	2.7123(15)
Cd1	O4 ⁴	2.379(4)	Cd3	O2 ¹¹	2.445(4)
Cd1	O5	2.319(4)	Cd3	O3	2.219(4)
Cd1	O5 ⁵	2.319(4)	Cd3	O4 ¹²	2.519(4)
Cd1	O6 ¹	2.540(4)	Cd3	O6	2.227(4)
Cd1	O6 ²	2.540(4)	Se1	O1	1.676(4)
Cd2	O1	2.287(4)	Se1	O4	1.694(4)
Cd2	O2 ⁶	2.267(4)	Se1	O6	1.733(4)
Cd2	O3 ⁷	2.292(4)	Se2	O2	1.697(4)
Cd2	O5 ⁸	2.284(4)	Se2	O3	1.721(4)
Cd2	O6 ⁹	2.328(4)	Se2	O5	1.681(4)
Cd3	Br1 ¹⁰	2.7152(13)			

¹1-X,1-Y,1-Z; ²+X,1-Y,-1/2+Z; ³1-X,2-Y,1-Z; ⁴+X,2-Y,-1/2+Z; ⁵1-X,+Y,1/2-Z; ⁶+X,1-Y,1/2+Z; ⁷1-X,1+Y,3/2-Z; ⁸+X,2-Y,1/2+Z; ⁹1-X,+Y,3/2-Z; ¹⁰1/2-X,3/2-Y,1-Z; ¹¹+X,1+Y,+Z; ¹²+X,-1+Y,+Z; ¹³1/2-X,1/2-Y,1-Z

Table S3. Selected bond angles [deg] for Cd₅Se₄O₁₂Cl₂.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2 ¹	Cd1	O2 ²	119.32(12)	O4	Cd2	O2 ⁷	82.92(10)
O3	Cd1	O2 ²	119.10(10)	O6 ⁹	Cd2	O1 ⁶	112.09(10)
O3	Cd1	O2 ¹	79.08(10)	O6 ⁹	Cd2	O2 ⁷	109.81(10)
O3 ³	Cd1	O2 ²	119.10(10)	O6 ⁹	Cd2	O3 ⁸	119.87(11)
O3 ³	Cd1	O2 ¹	79.08(10)	O6 ⁹	Cd2	O4	82.14(11)
O3 ³	Cd1	O3	145.83(14)	Cl1	Cd3	Cl1 ¹⁰	85.12(7)
O3	Cd1	O4 ¹	137.82(10)	Cl1	Cd3	Cl2 ¹⁰	60.27(6)
O3	Cd1	O4 ²	71.95(10)	O1	Cd3	Cl1 ¹⁰	89.47(8)
O3 ³	Cd1	O4 ¹	71.95(9)	O1	Cd3	Cl1	132.53(9)
O3 ³	Cd1	O4 ²	137.82(10)	O1	Cd3	Cl2 ¹⁰	142.11(8)
O3 ³	Cd1	O5 ⁴	86.00(10)	O1	Cd3	O6 ¹²	82.77(8)
O3 ³	Cd1	O5 ⁵	71.78(10)	O2	Cd3	Cl1	122.91(10)
O3	Cd1	O5 ⁵	71.78(10)	O2	Cd3	Cl1 ¹⁰	79.92(9)
O3	Cd1	O5 ⁴	86.00(11)	O2	Cd3	Cl2	75.74(10)
O4 ¹	Cd1	O2 ²	75.49(9)	O2	Cd3	Cl2 ¹⁰	92.46(8)
O4 ¹	Cd1	O2 ¹	60.62(9)	O2	Cd3	O5 ¹¹	134.24(8)
O4 ²	Cd1	O2 ²	60.62(9)	O2	Cd3	O6 ¹²	145.31(8)
O4 ²	Cd1	O2 ¹	75.49(9)	O5 ¹¹	Cd3	Cl1 ¹⁰	85.83(8)
O4 ¹	Cd1	O4 ²	85.60(14)	O5 ¹¹	Cd3	Cl1	75.29(9)
O5 ⁵	Cd1	O2 ¹	164.36(9)	O5 ¹¹	Cd3	Cl2 ¹⁰	78.95(10)
O5 ⁴	Cd1	O2 ¹	164.36(9)	O5 ¹¹	Cd3	Cl2	147.75(8)
O5 ⁴	Cd1	O2 ²	72.22(9)	O6 ¹²	Cd3	Cl1	80.17(8)
O5 ⁵	Cd1	O2 ²	72.22(9)	O6 ¹²	Cd3	Cl1 ¹⁰	135.30(8)
O5 ⁴	Cd1	O4 ²	134.96(9)	O6 ¹²	Cd3	Cl2 ¹⁰	88.56(8)
O5 ⁵	Cd1	O4 ¹	104.39(10)	O6 ¹²	Cd3	Cl2	147.77(8)
O5 ⁴	Cd1	O4 ¹	134.96(9)	O6 ¹²	Cd3	O5 ¹¹	79.37(9)
O5 ⁵	Cd1	O4 ²	104.39(10)	O4	Se1	O2	95.74(14)
O5 ⁵	Cd1	O5 ⁴	98.78(14)	O4	Se1	O5	105.99(14)
O1 ⁶	Cd2	O2 ⁷	89.91(10)	O5	Se1	O2	97.55(13)
O1 ⁶	Cd2	O3 ⁸	89.05(10)	O3	Se2	O1	95.18(14)
O1 ⁶	Cd2	O4	165.62(10)	O3	Se2	O6	102.84(15)
O3 ⁸	Cd2	O2 ⁷	126.52(10)	O6	Se2	O1	98.17(14)
O3 ⁸	Cd2	O4	85.28(11)				

¹+X,1-Y,1/2+Z; ²1-X,1-Y,1-Z; ³1-X,+Y,3/2-Z; ⁴+X,-Y,1/2+Z; ⁵1-X,-Y,1-Z; ⁶1-X,-1+Y,1/2-Z; ⁷1-X,+Y,1/2-Z; ⁸+X,-Y,-1/2+Z; ⁹+X,1-Y,-1/2+Z; ¹⁰3/2-X,1/2-Y,1-Z; ¹¹+X,1+Y,+Z; ¹²+X,-1+Y,+Z; ¹³3/2-X,3/2-Y,1-Z; ¹⁴1-X,1+Y,1/2-Z

Table S4. Selected bond angles [deg] for Cd₅Se₄O₁₂Br₂.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1 ¹	Cd1	O1 ²	85.2(2)	O2 ⁸	Cd2	O1	81.39(15)
O1 ²	Cd1	O6 ¹	75.18(13)	O2 ⁸	Cd2	O3 ⁶	113.39(14)
O1 ²	Cd1	O6 ²	60.83(12)	O2 ⁸	Cd2	O5 ⁹	119.62(15)
O1 ¹	Cd1	O6 ²	75.18(13)	O2 ⁸	Cd2	O6 ⁷	109.71(14)
O1 ¹	Cd1	O6 ¹	60.83(12)	O3 ⁶	Cd2	O6 ⁷	90.62(15)
O4 ³	Cd1	O1 ¹	105.17(14)	O5 ⁹	Cd2	O1	85.36(16)
O4 ³	Cd1	O1 ²	134.54(13)	O5 ⁹	Cd2	O3 ⁶	87.90(15)
O4 ⁴	Cd1	O1 ²	105.17(14)	O5 ⁹	Cd2	O6 ⁷	126.61(14)
O4 ⁴	Cd1	O1 ¹	134.54(13)	O3	Cd3	Br1	133.25(11)
O4 ⁴	Cd1	O4 ³	98.33(19)	O3	Cd3	Br2	83.40(11)
O4 ⁴	Cd1	O6 ²	72.32(13)	O3	Cd3	Br2 ¹⁰	141.79(10)
O4 ³	Cd1	O6 ¹	72.32(13)	O3	Cd3	O2 ¹¹	75.74(14)
O4 ⁴	Cd1	O6 ¹	164.53(12)	O3	Cd3	O4 ¹²	78.68(13)
O4 ³	Cd1	O6 ²	164.53(12)	O3	Cd3	O6	121.57(14)
O5 ⁵	Cd1	O1 ²	72.24(14)	O4 ¹²	Cd3	Br1 ¹⁰	148.08(9)
O5	Cd1	O1 ²	138.27(14)	O4 ¹²	Cd3	Br1	81.01(10)
O5	Cd1	O1 ¹	72.24(14)	O4 ¹²	Cd3	Br2 ¹⁰	137.24(10)
O5 ⁵	Cd1	O1 ¹	138.27(14)	O4 ¹²	Cd3	Br2	88.90(10)
O5	Cd1	O4 ³	85.98(15)	O6	Cd3	Br1	92.57(10)
O5 ⁵	Cd1	O4 ³	71.22(14)	O6	Cd3	Br1 ¹⁰	134.93(11)
O5	Cd1	O4 ⁴	71.23(14)	O6	Cd3	Br2	145.69(10)
O5 ⁵	Cd1	O4 ⁴	85.98(15)	O6	Cd3	Br2 ¹⁰	86.78(11)
O5 ⁵	Cd1	O5	145.1(2)	O6	Cd3	O2 ¹¹	77.36(14)
O5	Cd1	O6 ¹	119.14(14)	O6	Cd3	O4 ¹²	75.20(14)
O5	Cd1	O6 ²	79.37(14)	O4	Se1	O6	97.03(19)
O6 ¹	Cd1	O6 ²	119.38(17)	O2	Se2	O3	97.62(19)
O1	Cd2	O3 ⁶	165.17(14)	O5	Se2	O2	103.0(2)
O1	Cd2	O6 ⁷	82.87(15)	O5	Se2	O3	94.85(19)

¹+X,1-Y,-1/2+Z; ²1-X,1-Y,1-Z; ³1-X,2-Y,1-Z; ⁴+X,2-Y,-1/2+Z; ⁵1-X,+Y,1/2-Z; ⁶1-X,1+Y,3/2-Z;
⁷+X,2-Y,1/2+Z; ⁸1-X,+Y,3/2-Z; ⁹+X,1-Y,1/2+Z; ¹⁰1/2-X,3/2-Y,1-Z; ¹¹+X,1+Y,+Z; ¹²+X,-1+Y,+Z;
¹³1/2-X,1/2-Y,1-Z; ¹⁴1-X,-1+Y,3/2-Z

Table S5. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Cd}_5\text{Se}_4\text{O}_{12}\text{Cl}_2$.

Atom	Wyckoff	<i>x</i>	<i>y</i>	<i>z</i>	$U_{(\text{eq})}$	$BVS^{[a]}$
Cd1	4 <i>e</i>	5000	7988.1(7)	7500	13.4(1)	2.008
Cd2	8 <i>f</i>	5047.9(2)	-2751.8(5)	926.0(2)	15.66(8)	2.004
Cd3	8 <i>f</i>	6440.0(2)	2509.4(5)	4609.2(2)	15.79(8)	1.960
Se1	8 <i>f</i>	6266.0(2)	-2381.8(6)	3139.0(2)	12.94(9)	3.850
Se2	8 <i>f</i>	6120.1(2)	7514.9(7)	5960.0(2)	15.55(10)	3.853
O1	8 <i>f</i>	5852.3(15)	5473(5)	5133.7(17)	18.1(5)	1.989
O2	8 <i>f</i>	5845.8(15)	-378(5)	3690.2(17)	17.8(5)	2.086
O3	8 <i>f</i>	5441.6(17)	6704(5)	6391.7(19)	25.0(6)	2.002
O4	8 <i>f</i>	5782.6(17)	-1411(5)	2192.9(17)	24.2(6)	1.949
O5	8 <i>f</i>	5858.5(16)	-5079(5)	3321.2(17)	21.8(6)	1.788
O6	8 <i>f</i>	5794.9(19)	10199(5)	5443.7(19)	29.1(7)	1.943
Cl1	8 <i>f</i>	7535.0(11)	2688(4)	3954.4(13)	24.2(5)	0.691
Cl2	8 <i>f</i>	7503.6(10)	5780(4)	4956.7(13)	25.2(6)	0.711
GII = 0.153^[b]						

[a] The bond valence sum is calculated by bond-valence theory ($S_i = \exp[(R_o - R_i)/B]$, where R_o is an empirical constant, R_i is the length of bond (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 0.153, which is lower than 0.2 indicating the rationality of the structure from this side.

Table S6. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Cd}_5\text{Se}_4\text{O}_{12}\text{Br}_2$.

Atom	Wyckoff	x	y	z	$U_{\text{(eq)}}$	$BVS^{\text{[a]}}$
Cd1	4e	5000	2070.1(10)	2500	12.87(13)	2.005
Cd2	8f	4970.4(2)	12703.7(7)	9087.6(2)	14.49(11)	1.747
Cd3	8f	3575.9(2)	7492.3(8)	5404.3(3)	17.87(12)	1.960
Se1	8f	3770.2(3)	12330.1(9)	6899.5(3)	12.40(13)	3.791
Se2	8f	3914.8(3)	2527.6(10)	4052.2(3)	14.09(13)	3.798
O1	8f	4255(2)	11338(8)	7837(2)	23.4(9)	1.914
O2	8f	4238(2)	-132(7)	4582(3)	22.8(9)	1.882
O3	8f	4159(2)	4584(7)	4879(2)	18.0(8)	1.975
O4	8f	4167(2)	15010(7)	6695(2)	20.3(8)	1.761
O5	8f	4582(2)	3374(8)	3624(3)	23.9(9)	2.009
O6	8f	4160(2)	10336(7)	6316(2)	18.4(8)	2.075
Br1	8f	2459.3(6)	7310(2)	6122.3(7)	29.9(3)	0.679
Br2	8f	2494.3(8)	4073(3)	5054.2(10)	25.1(4)	0.750
GII = 0.182^[b]						

[a] The bond valence sum is calculated by bond-valence theory ($S_i = \exp[(R_o - R_i)/B]$, where R_o is an empirical constant, R_i is the length of the bond (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 structure's rationality from this side.

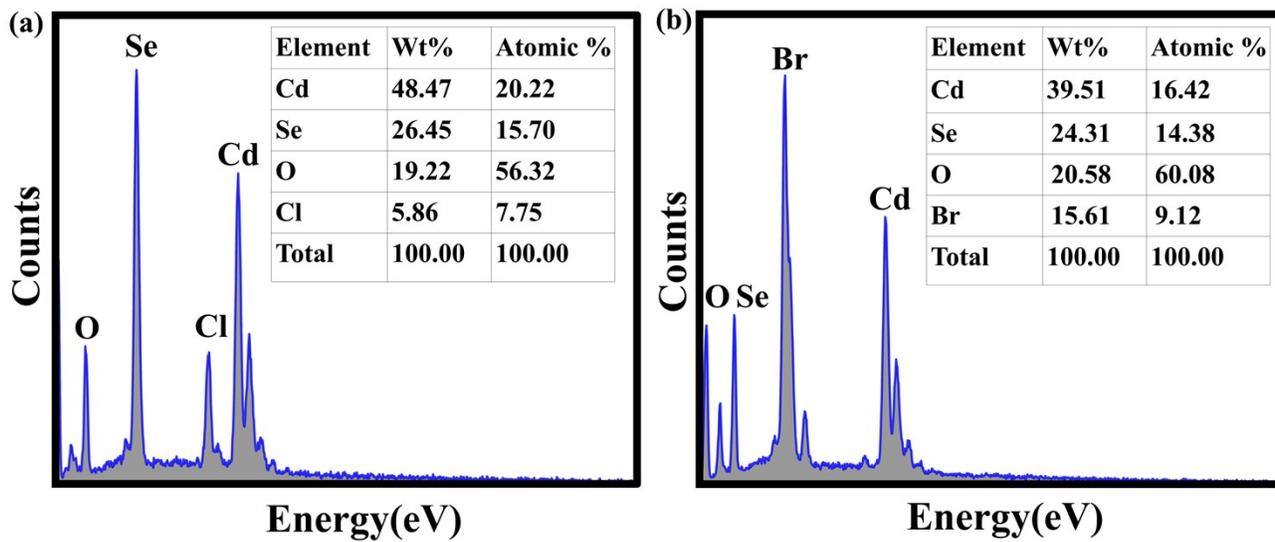


Figure S1. Energy-dispersive X-ray spectroscopy (EDS) analyses for (a) $\text{Cd}_5\text{Se}_4\text{O}_{12}\text{Cl}_2$, and (b) $\text{Cd}_5\text{Se}_4\text{O}_{12}\text{Br}_2$.

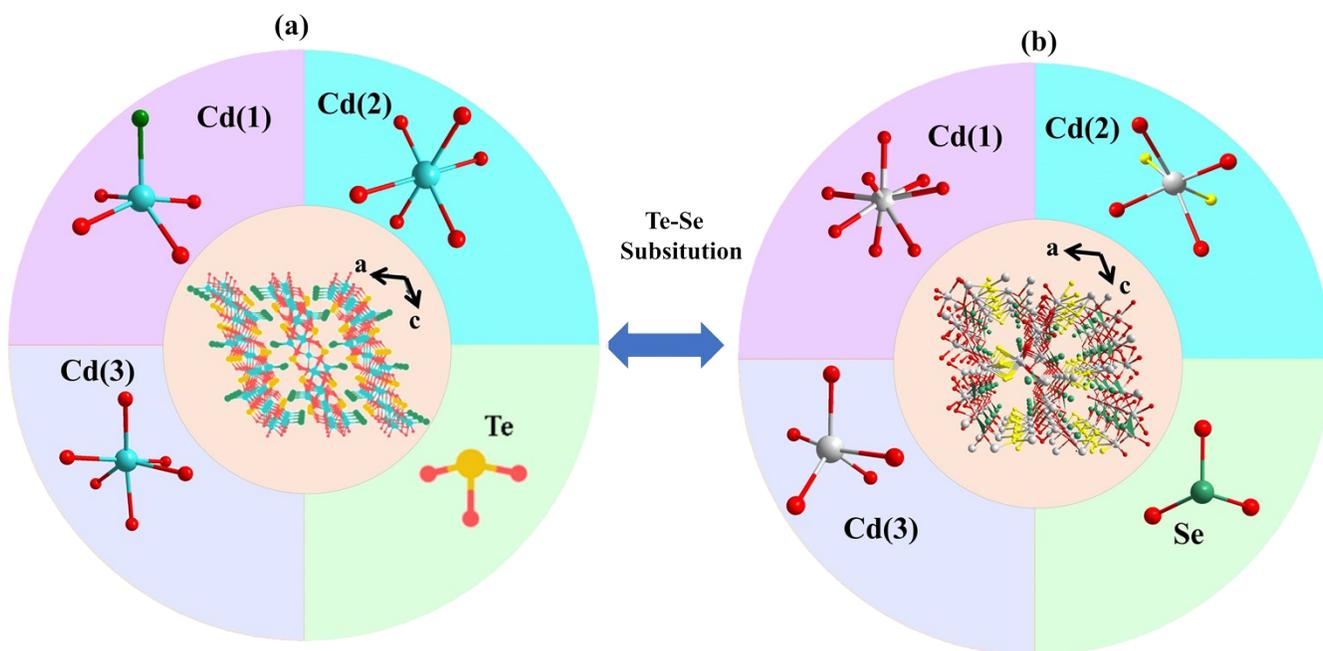


Figure S2. Coordination geometries of Cd(1), Cd(2), Cd(3), and Te/Se atoms in $P2_1/c$ - $\text{Cd}_5\text{Te}_4\text{O}_{12}\text{X}_2$, (X = Cl, Br, I) (a) and $C2/c$ - $\text{Cd}_5\text{Se}_4\text{O}_{12}\text{X}_2$, (X = Cl, Br) (b).

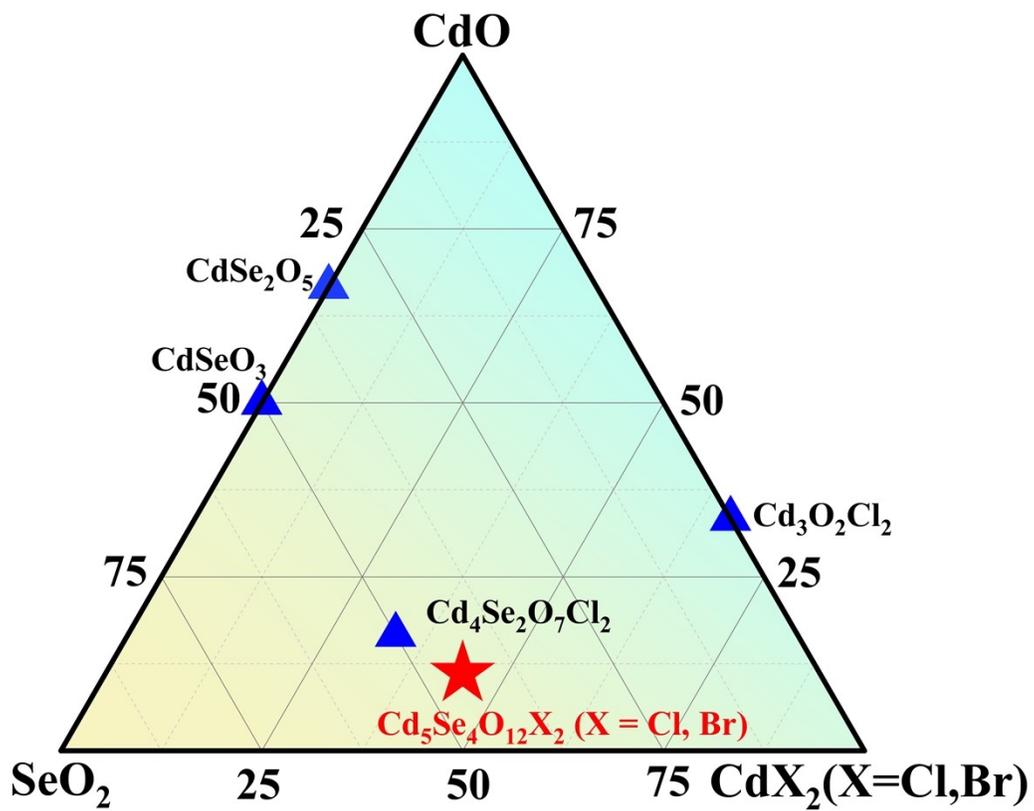


Figure S3. pseudo-ternary diagram of the CdO-SeO₂-CdX₂ (X=Cl/Br) system.

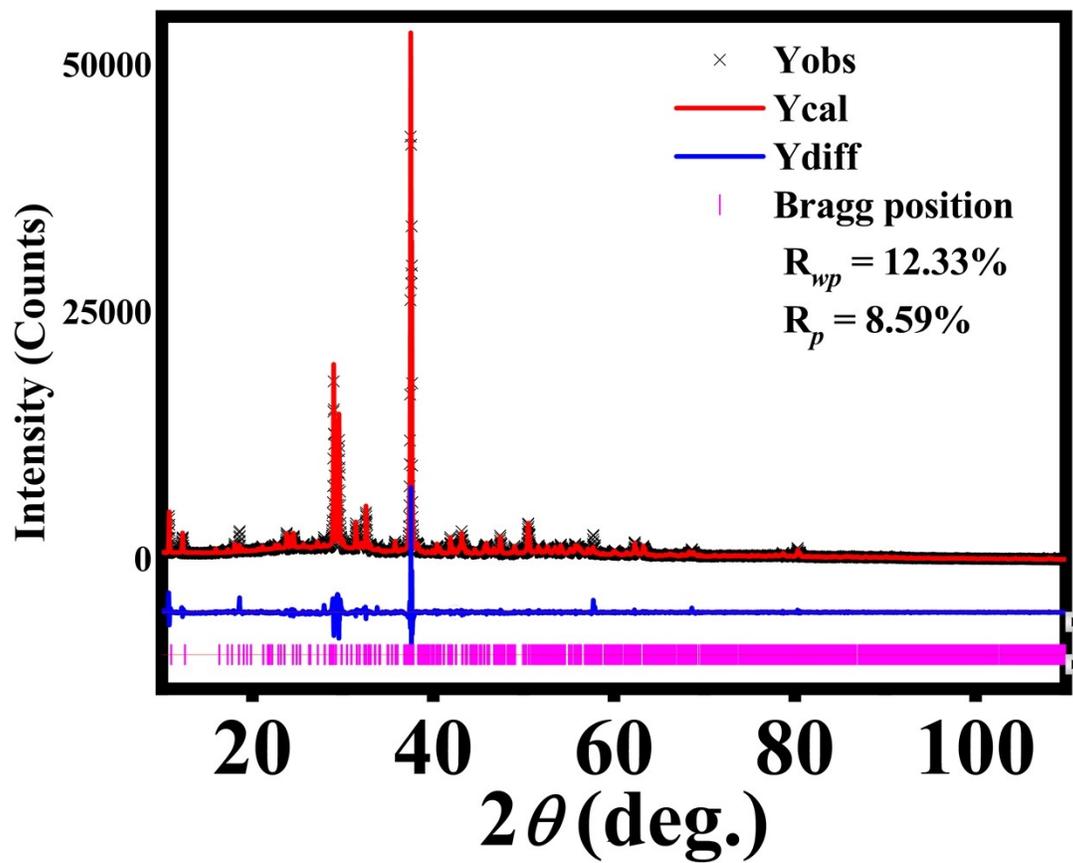


Figure S4. Experimental and Rietveld refinement XRD patterns of $\text{Cd}_5\text{Se}_4\text{O}_{12}\text{Br}_2$.