Electronic Supplementary Information

Ultralow thermal conductivity in the quaternary semiconducting chalcogenide Cs$_4$[Ho$_{26}$Cd$_7$Se$_{48}$] with an unprecedented closed cavity architecture

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Supporting Information Index

1. Experimental Section

1.1 Materials and Instruments

1.2 Synthesis

1.3 Crystal Structure Determinations

2. Computational Section

3. Figures and Tables

Fig. S1 Coordination geometry of Cs$_4$[Ho$_{26}$Cd$_7$Se$_{48}$].

Fig. S2 Coordination geometry of Cs atom in the structure of Cs$_4$[Ho$_{26}$Cd$_7$Se$_{48}$] with Cs–Se distances marked.

Fig. S3 Experimental (black) and simulated (red) powder XRD patterns of Cs$_4$[Ho$_{26}$Cd$_7$Se$_{48}$].

Fig. S4 EDX results of Cs$_4$[Ho$_{26}$Cd$_7$Se$_{48}$].

Fig. S5 TG diagram of Cs$_4$[Ho$_{26}$Cd$_7$Se$_{48}$].

Fig. S6 SEM image of the fractured surface obtained from the hot-pressed pellet of Cs$_4$[Ho$_{26}$Cd$_7$Se$_{48}$].

Fig. S7 Calculated band structure of $Cs_4[Ho_{26}Cd_7Se_{48}]$.

Fig. S8 Electrical conductivity (σ) as a function of temperature for $Cs_4[Ho_{26}Cd_7Se_{48}]$ using a K2500-5RSLP Variable Temperature Hall Measurement system.

Fig. S9 Temperature dependence of the atomic displacement parameter (ADP) values from 100 to 300 K for $Cs_4[Ho_{26}Cd_7Se_{48}]$.

Table S1. Crystallographic data and refinement details for $Cs_4[RE_{26}Cd_7Se_{48}]$ (RE = Ho, Er, Tm, and Lu).

Table S2-1. Atomic coordinates and equivalent isotropic displacement parameters of $Cs_4[Ho_{26}Cd_7Se_{48}]$.

Table S2-2. Atomic coordinates and equivalent isotropic displacement parameters of $Cs_4[Er_{26}Cd_7Se_{48}]$.

Table S2-3. Atomic coordinates and equivalent isotropic displacement parameters of $Cs_4[Tm_{26}Cd_7Se_{48}]$.

Table S2-4. Atomic coordinates and equivalent isotropic displacement parameters of $Cs_4[Lu_{26}Cd_7Se_{48}]$.

Table S3. Selected bond lengths (Å) of $Cs_4[RE_{26}Cd_7Se_{48}]$ (RE = Ho, Er, Tm, and Lu).

Table S4. EDX results of $Cs_4[Tm_{26}Cd_7Se_{48}]$.

4. References

1. Experimental Section

1.1 Materials and Instruments

All of the chemicals were obtained from commercial sources and used without further purification. Chunks of Ho, Er, Tm, and Lu, (99.95%) were purchased from Huhhot Jinrui Rare Earth Co., Ltd. Granular Cd (99.99%) and Lumpy Se (99.99%) were purchased from Alfa Aesar, and powdery CsCl (99.9%) was

purchased from Sinopharm Chemical Reagent Co., Ltd. Powder X-ray diffraction (XRD) patterns were collected on a Rigaku Mini-Flex II powder diffractometer by using Cu-K$_\alpha$ radiation (λ = 1.5416 Å) at room temperature. Elemental analysis was carried out using a field emission scanning electron microscope (FESEM, JSM6700F) equipped with an energy dispersive X-ray (EDX) spectrometer (Oxford INCA). Diffuse-reflectance spectra were recorded at room temperature using an UV−Vis−NIR spectrometer (Perkin-Elmer Lambda 950). The reflectance spectrum of the BaSO$_4$ powder was collected as the baseline.[1] The thermal stability analyses were measured on a NETZSCH STA 449C simultaneous analyzer. The magnetic property was measured on a Quantum Design PPMS-9T magnetometer in the temperature range of 2–300 K. The thermal conductivity were measured by laser flash techniques with a Netzsch LFA 457 system and calculated using the formula $\kappa = D \times C_p \times d$, where D was the measured thermal diffusivity, C_p was the heat capacity estimated using the Dulong-Petit model (C_p = 3nR, where n is the number of atoms per formula unit and R is the gas constant) and d was the sample density.[2] The uncertainty of the thermal conductivity k is estimated to be within 5%, considering the uncertainties for D, C_p and d. Electrical conductivity (σ) was measured on a K2500-5RSLP Variable Temperature Hall Measurement System.

1.2 Syntheses

Cs$_4$[RE$_{26}$Cd$_7$Se$_{48}$] (RE = Ho, Er, Tm, and Lu). Reactants were stored in an Ar-filled glovebox with controlled oxygen and moisture levels below 0.1 ppm. These

compounds were obtained by a high-temperature solid-state method with CsCl, RE, Cd and Se as the raw materials. The reagents were mixed in a mole ratio of CsCl: RE: Cd: Se = 5:26:7:48, and then sealed in an evacuated silica tube and annealed in tube furnaces with controlled temperature. The mixture was heated to 1223 K at 10 K/h and maintained there for 4 days, followed by slow cooling to room temperature at 3 K/h. The reacting product was washed with deionized water and ethanol and dried in air. The yellowish brown granular crystals were obtained in the yields of 30–90% based on RE. The exact composition of the compound was established from the X-ray structure refinement. Semi-quantitative EDX analyses carried out on several single crystals revealed the presence of Cs, RE, Cd and Se in a ratio closes to the chemical formula of the title compounds. No other element was detected.

The as-synthesized polycrystalline samples were ground into a fine powder and hot-pressed pellets (at 723 K for 60 min under an axial compressive stress of 100 MPa in vacuum) with a theoretical density of more than 90% were used for thermal conductivity measurements.

1.3 Crystal Structure Determinations

All data collections were performed on a Mercury 70 CCD diffractometer equipped with graphite-monochromated Mo K_α radiation (λ = 0.71073 Å) at 293 K. Absorption corrections were performed by the multi-scan method.[3] All structure were solved by the direct methods and refined by the full-matrix least-squares fitting on F^2 by *SHELX–2014*.[4] For simplicity, take $Cs_4[Ho_{26}Cd_7Se_{48}]$ for example, initially one Cs, twelve Se, and nine "M" metal sites were distinguished according to their bond

distances and coordination environments. For example, the coordination polyhedra around metal sites M1–8 are distorted octahedra with 6 Se atoms ($d_{M–S}$ = 2.7354–2.9570 Å) and these sites are tentatively referred to as "Ho" atoms. While metal site M9 is 100% Cd and is coordinated with 4 Se atoms in a regular tetrahedron ($d_{M–S}$ = 2.6501 Å). After refinement the *R* values were *R*1 = 14.32% and *wR*2 = 34.65%. In a subsequent step the occupancy of the 8 "Ho" atoms was free refined (*R*1 = 7.22%, *wR*2 = 19.31%). Among them, the occupancy of four sites was almost unchanged, that is close to 100%, while for the remaining four sites, the occupancy dropped to less than 0.5 (full theoretical occupancy). According to the EDX results, Ho and Cd were constrained to share the same crystallographic site and freely refined their occupancies by using "EXYZ" and "EADP" commands in these four sites. The formula at that point was $Cs_4[Ho_{26.03}Cd_{6.97}Se_{48}]$; however, for charge balancing purposes the compound should have the general formula $Cs_4[Ho_{26}Cd_7Se_{48}]$, which is agreement with the EDX data. All atoms were refined anisotropically (*R*1 = 5.31%, *wR*2 = 12.65%). Crystallographic data and structural refinement details were summarized in Table S1, the positional coordinates and isotropic equivalent thermal parameters were given in Table S2, and some important bond distances were listed in Table S3.
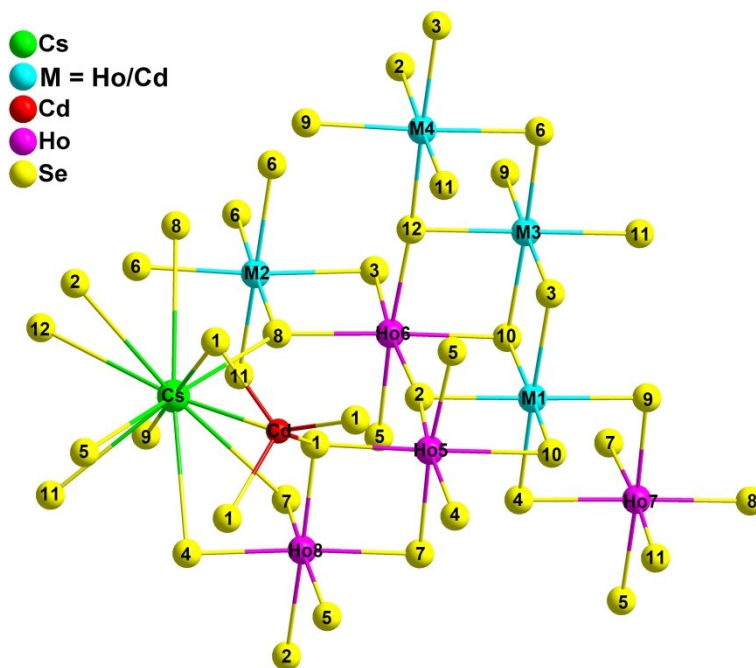
2. Computational Section

The geometry optimization, band structure and density of states (DOS) were calculated by the *Vienna ab initio simulation package* (VASP).[5] The generalized

gradient approximation (GGA)[6] was chosen as the exchange–correlation functional and a plane wave basis with the projector augmented wave (PAW)[7,8] potentials was used. The plane-wave cut-off energy of 500 eV, and a threshold of 10^{-6} eV were set for the self-consistent-field convergence of the total electronic energy. The Fermi level ($E_F = 0$ eV) was selected as the reference of the energy. The 4f electrons of the Ho element were treated as core electrons.

Fig. S1 Coordination geometry of $Cs_4[Ho_{26}Cd_7Se_{48}]$.

Fig. S2 Coordination geometry of Cs atom in the structure of $Cs_4[Ho_{26}Cd_7Se_{48}]$ with Cs–Se distances marked.

Fig. S3 Experimental (black) and simulated (red) powder XRD patterns of $Cs_4[Ho_{26}Cd_7Se_{48}]$.

Atomic %	Cs	Ho	Cd	Se
Single cryst.	4	26	7	48
EDX (ave.)	4	26.3(4)	6.9(1)	48.6(5)

Fig. S4 EDX results of $Cs_4[Ho_{26}Cd_7Se_{48}]$.

Fig. S5 TG diagram of $Cs_4[Ho_{26}Cd_7Se_{48}]$.

Fig. S6 SEM image of the fractured surface obtained from the hot-pressed pellet of $Cs_4[Ho_{26}Cd_7Se_{48}]$.

Fig. S7 Calculated band structure of $Cs_4[Ho_{26}Cd_7Se_{48}]$.

Fig. S8 Electrical conductivity (σ) as a function of temperature for $Cs_4[Ho_{26}Cd_7Se_{48}]$

using a K2500-5RSLP Variable Temperature Hall Measurement system.

Fig. S9 Temperature dependence of the atomic displacement parameter (ADP) values from 100 to 300 K for $Cs_4[Ho_{26}Cd_7Se_{48}]$. The largest ADP of Cs in $Cs_4[Ho_{26}Cd_7Se_{48}]$ is regarded as an evidence of rattling mode.

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Electronic Supplementary Information

Table S1. Crystallographic data and refinement details for $Cs_4[RE_{26}Cd_7Se_{48}]$ (RE = Ho, Er, Tm, and Lu).

Formula	$Cs_4[Ho_{26}Cd_7Se_{48}]$	$Cs_4[Er_{26}Cd_7Se_{48}]$	$Cs_4[Tm_{26}Cd_7Se_{48}]$	$Cs_4[Lu_{26}Cd_7Se_{48}]$
Fw	9396.70	9457.28	9500.70	9657.74
Temperature(K)		293(2)		
Crystal system		tetragonal		
Space group		$I4_1/a$ (No. 88)		
a (Å)	20.667(7)	20.513(5)	20.5073(3)	20.3890(8)
b (Å)	20.667(7)	20.513(5)	20.5073(3)	20.3890(8)
c (Å)	22.816(10)	22.655(7)	22.6556(5)	22.4797(14)
α (deg.)	90	90	90	90
β (deg.)	90	90	90	90
γ (deg.)	90	90	90	90
V (Å^3)	9746(8)	9533(6)	9527.8(3)	9345.1(9)
Z		4		
D_c (g cm^{-3})	6.40	6.59	6.62	6.86
μ (mm^{-1})	41.7	43.9	45.3	48.9
GOOF on F^2	1.082	1.047	1.085	1.033
R_1, wR$_2$ ($I > 2\sigma(I)$)	0.0531, 0.1264	0.0392, 0.1034	0.0298, 0.0655	0.0384, 0.0881
R_1, wR$_2$ (all data)	0.0605, 0.1323	0.0461, 0.1088	0.0384, 0.0681	0.0474, 0.0939
diff peak, hole (e. Å^{-3})	4.13, −3.51	2.53, −2.91	3.18, −3.68	2.60, −3.28

Electronic Supplementary Information

Table S2-1. Atomic coordinates and equivalent isotropic displacement parameters of

$Cs_4[Ho_{26}Cd_7Se_{48}]$.

Atom	*Wyck.*	x	y	z	$U_{(eq)}(Å^2)^*$	Occu.
Cs	16f	0.60738(6)	0.22805(6)	0.06400(6)	0.0401(3)	1.0
M1 = Ho1/Cd1	16f	0.25148(3)	-0.00261(4)	0.06184(3)	0.0151(2)	0.67(2)/0.33(2)
M2 = Ho2/Cd2	16f	0.48323(4)	0.15484(4)	0.30693(4)	0.0152(2)	0.45(2)/0.55(2)
M3 = Ho3/Cd3	16f	0.17344(4)	0.11513(4)	0.18813(4)	0.0169(2)	0.57(2)/0.43(2)
M4 = Ho4/Cd4	16f	0.21430(3)	0.30653(3)	0.18540(3)	0.01009(19)	0.91(2)/0.09(2)
Cd5	4b	0.5	0.25	-0.1250	0.0217(5)	1.0
Ho5	16f	0.36959(3)	0.08510(3)	-0.06035(3)	0.00868(18)	1.0
Ho6	16f	0.36953(3)	0.08102(3)	0.18487(3)	0.00931(18)	1.0
Ho7	16f	0.20953(3)	-0.19241(3)	0.06306(3)	0.00777(18)	1.0
Ho8	16f	0.55691(3)	0.04598(3)	-0.06000(3)	0.00744(17)	1.0
Se1	16f	0.48161(6)	0.15639(6)	-0.04669(7)	0.0145(3)	1.0
Se2	16f	0.36338(6)	0.07120(6)	0.06149(6)	0.0102(3)	1.0
Se3	16f	0.16998(6)	0.11342(6)	0.06030(6)	0.0090(3)	1.0
Se4	16f	0.32684(6)	-0.11809(6)	0.06384(6)	0.0116(3)	1.0
Se5	16f	0.28635(6)	0.19357(6)	-0.06516(5)	0.0074(3)	1.0
Se6	16f	0.48174(6)	0.15179(6)	0.43211(7)	0.0113(3)	1.0
Se7	16f	0.44193(6)	-0.03120(6)	-0.06366(5)	0.0068(3)	1.0
Se8	16f	0.48252(6)	0.15236(6)	0.18608(6)	0.0136(4)	1.0
Se9	16f	0.13744(6)	-0.07560(6)	0.06232(6)	0.0123(3)	1.0
Se10	16f	0.25584(6)	0.00065(6)	0.18624(5)	0.0089(3)	1.0
Se11	16f	0.56131(6)	0.03985(6)	0.31162(6)	0.0129(3)	1.0
Se12	16f	0.28603(6)	0.19104(6)	0.18849(6)	0.0105(3)	1.0

$^*U_{(eq)}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S2-2. Atomic coordinates and equivalent isotropic displacement parameters of

$Cs_4[Er_{26}Cd_7Se_{48}]$.

Atom	*Wyck.*	x	y	z	$U_{(eq)}(Å^2)^*$	Occu.
Cs	16f	0.02174(4)	0.14323(4)	0.31413(4)	0.0331(3)	1.0
M1 = Er1/Cd1	16f	0.24732(3)	0.00135(3)	0.18715(2)	0.01132(17)	0.71(2)/0.29(2)
M2 = Er2/ Cd2	16f	0.09507(3)	0.26707(3)	0.55739(3)	0.00879(18)	0.31(2)/0.69(2)
M3 = Er3/ Cd3	16f	0.13468(3)	0.07709(3)	0.56142(2)	0.01133(16)	0.62(2)/0.38(2)
M4 = Er4/ Cd4	16f	0.05651(2)	-0.03571(2)	0.43490(2)	0.00643(15)	0.90(2)/0.10(2)
Cd5	4b	0	0.25	0.1250	0.0140(3)	1.0
Er5	16f	0.13019(2)	0.08478(2)	0.06004(2)	0.00446(14)	1.0
Er6	16f	0.33092(2)	0.11946(2)	0.06439(2)	0.00565(14)	1.0
Er7	16f	0.29027(2)	0.30739(2)	0.06307(2)	0.00420(14)	1.0
Er8	16f	0.20439(2)	0.19313(2)	0.18965(2)	0.00366(14)	1.0
Se1	16f	0.01830(5)	0.15593(5)	0.04645(6)	0.0092(2)	1.0
Se2	16f	0.32118(5)	0.11347(5)	0.18740(4)	0.0069(3)	1.0
Se3	16f	0.32986(5)	0.11324(5)	-0.06168(4)	0.0073(3)	1.0
Se4	16f	0.13185(5)	0.07699(5)	0.18492(4)	0.0083(3)	1.0
Se5	16f	0.21346(5)	0.19319(5)	0.06447(4)	0.0050(3)	1.0
Se6	16f	0.01816(5)	0.15156(5)	0.56694(5)	0.0093(3)	1.0
Se7	16f	0.21853(5)	0.19187(5)	0.31299(4)	0.0046(2)	1.0
Se8	16f	0.40208(5)	0.23243(5)	0.06493(5)	0.0127(3)	1.0
Se9	16f	0.13725(5)	0.07606(5)	0.43656(4)	0.0090(3)	1.0
Se10	16f	0.25068(5)	0.00568(5)	0.06196(4)	0.0063(3)	1.0
Se11	16f	0.21054(5)	0.18923(5)	0.56092(4)	0.0096(3)	1.0
Se12	16f	0.44106(5)	0.03645(5)	0.06055(4)	0.0078(3)	1.0

$^*U_{(eq)}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Electronic Supplementary Information

Table S2-3. Atomic coordinates and equivalent isotropic displacement parameters of

$Cs_4[Tm_{26}Cd_7Se_{48}]$.

Atom	Wyck.	x	y	z	$U_{(eq)}(Å^2)^*$	Occu.
Cs	16f	0.02180(3)	0.14323(3)	0.31405(3)	0.03329(15)	1.0
M1 = Tm1/Cd1	16f	0.24733(2)	0.00129(2)	0.18707(2)	0.01273(9)	0.70(2)/0.30(2)
M2 = Tm2/Cd2	16f	0.09494(2)	0.26708(2)	0.55748(2)	0.01074(10)	0.33(2)/0.67(2)
M3 = Tm3/Cd3	16f	0.13469(2)	0.07717(2)	0.56152(2)	0.01226(9)	0.63(2)/0.37(2)
M4 = Tm4/Cd4	16f	0.05647(2)	-0.03574(2)	0.43481(2)	0.00801(8)	0.90(2)/0.10(2)
Cd5	4b	0	0.25	0.1250	0.0145(2)	1.0
Tm5	16f	0.13023(2)	0.08477(2)	0.06000(2)	0.00659(7)	1.0
Tm6	16f	0.33097(2)	0.11947(2)	0.06439(2)	0.00766(8)	1.0
Tm7	16f	0.29027(2)	0.30739(2)	0.06306(2)	0.00616(7)	1.0
Tm8	16f	0.20446(2)	0.19313(2)	0.18965(2)	0.00569(7)	1.0
Se1	16f	0.01842(3)	0.15597(3)	0.04651(3)	0.01009(14)	1.0
Se2	16f	0.32121(3)	0.11345(3)	0.18737(3)	0.00753(14)	1.0
Se3	16f	0.32989(3)	0.11326(3)	-0.06174(3)	0.00700(15)	1.0
Se4	16f	0.13190(3)	0.07696(3)	0.18490(3)	0.00923(15)	1.0
Se5	16f	0.21350(3)	0.19317(3)	0.06448(3)	0.00559(13)	1.0
Se6	16f	0.01825(3)	0.15151(3)	0.56679(3)	0.00999(15)	1.0
Se7	16f	0.21849(3)	0.19184(3)	0.31309(3)	0.00540(13)	1.0
Se8	16f	0.40205(3)	0.23237(3)	0.06507(3)	0.01320(16)	1.0
Se9	16f	0.13735(3)	0.07603(3)	0.43666(3)	0.00947(15)	1.0
Se10	16f	0.25079(3)	0.00570(3)	0.06191(3)	0.00663(15)	1.0
Se11	16f	0.21055(3)	0.18933(3)	0.56100(3)	0.01057(14)	1.0
Se12	16f	0.44115(3)	0.03650(3)	0.06058(3)	0.00786(14)	1.0

$^*U_{(eq)}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Electronic Supplementary Information

Table S2-4. Atomic coordinates and equivalent isotropic displacement parameters of

$Cs_4[Lu_{26}Cd_7Se_{48}]$.

Atom	*Wyck.*	x	y	z	$U_{(eq)}$(Å^2)*	Occu.
Cs	16*f*	0.60632(5)	0.22841(5)	0.06440(4)	0.0301(2)	1.0
M1 = Lu1/Cd1	16*f*	0.25108(3)	-0.00270(3)	0.06213(3)	0.01145(16)	0.73(2)/0.27(2)
M2 = Lu2/Cd2	16*f*	0.48279(3)	0.15514(3)	0.30762(3)	0.00852(17)	0.27(2)/0.73(2)
M3 = Lu3/Cd3	16*f*	0.17247(3)	0.11545(3)	0.18776(3)	0.01094(16)	0.67(2)/0.33(2)
M4 = Lu4/Cd4	16*f*	0.21426(2)	0.30639(2)	0.18505(2)	0.00843(14)	0.91(2)/0.09(2)
Cd5	4*b*	0.5	0.25	-0.1250	0.0132(4)	1.0
Lu5	16*f*	0.37002(2)	0.08458(2)	-0.06046(2)	0.00599(13)	1.0
Lu6	16*f*	0.36928(2)	0.08095(2)	0.18532(2)	0.00658(13)	1.0
Lu7	16*f*	0.20977(2)	-0.19278(2)	0.06258(2)	0.00540(13)	1.0
Lu8	16*f*	0.55687(2)	0.04519(2)	-0.06028(2)	0.00477(13)	1.0
Se1	16*f*	0.48172(6)	0.15541(6)	-0.04631(6)	0.0095(3)	1.0
Se2	16*f*	0.36339(5)	0.07141(6)	0.06170(5)	0.0065(3)	1.0
Se3	16*f*	0.17010(5)	0.11319(5)	0.06071(5)	0.0062(3)	1.0
Se4	16*f*	0.32702(5)	-0.11801(6)	0.06406(5)	0.0089(3)	1.0
Se5	16*f*	0.28656(5)	0.19294(5)	-0.06496(5)	0.0046(2)	1.0
Se6	16*f*	0.48163(5)	0.15148(6)	0.43365(5)	0.0095(3)	1.0
Se7	16*f*	0.44176(5)	-0.03170(5)	-0.06360(5)	0.0042(2)	1.0
Se8	16*f*	0.48223(6)	0.15209(6)	0.18396(6)	0.0125(3)	1.0
Se9	16*f*	0.13727(5)	-0.07642(5)	0.06211(5)	0.0085(3)	1.0
Se10	16*f*	0.25532(5)	0.00085(5)	0.18658(5)	0.0062(3)	1.0
Se11	16*f*	0.56006(6)	0.03935(5)	0.31152(5)	0.0096(3)	1.0
Se12	16*f*	0.28662(5)	0.19115(5)	0.18890(5)	0.0082(3)	1.0

*$U_{(eq)}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S3. Selected bond lengths (Å) of $Cs_4[RE_{26}Cd_7Se_{48}]$ (RE = Ho, Er, Tm, and Lu).

	$Cs_4[Ho_{26}Cd_7Se_{48}]$	$Cs_4[Er_{26}Cd_7Se_{48}]$	$Cs_4[Tm_{26}Cd_7Se_{48}]$	$Cs_4[Lu_{26}Cd_7Se_{48}]$
M1–Se2	2.7705(18)	2.7541(14)	2.7544(7)	2.7435(12)
M1–Se9	2.7984(18)	2.7827(14)	2.7790(7)	2.7646(12)
M1–Se10	2.8406(18)	2.8321(14)	2.8307(7)	2.7997(14)
M1–Se4	2.8504(18)	2.8330(13)	2.8338(8)	2.8154(13)
M1–Se10	2.8714(18)	2.8385(13)	2.8380(8)	2.8275(13)
M1–Se3	2.9305(18)	2.9035(14)	2.9025(7)	2.8829(13)
M2–Se8	2.758(2)	2.384(6)	2.7772(8)	2.7805(14)
M2–Se6	2.857(2)	2.7716(15)	2.8496(8)	2.8343(14)
M2–Se6	2.8699(18)	2.8482(16)	2.8522(7)	2.8352(13)
M2–Se11	2.8745(18)	2.8549(14)	2.8582(8)	2.8396(13)
M2–Se6	2.8967(18)	2.8578(14)	2.8671(7)	2.8489(13)
M2–Se3	2.9204(18)	2.8683(14)	2.8996(7)	2.8817(13)
M3–Se11	3.9298(15)	2.7773(13)	2.7769(7)	2.7677(12)
M3–Se12	3.9502(15)	2.7998(13)	2.8023(7)	2.7929(12)
M3–Se9	2.7913(17)	2.8294(14)	2.8293(8)	2.7962(13)
M3–Se6	2.8064(18)	2.8394(13)	2.8355(7)	2.8094(13)
M3–Se3	2.834(2)	2.8759(14)	2.8724(7)	2.8568(12)
M3–Se10	2.8714(18)	2.9004(13)	2.8988(7)	2.8835(12)
M4–Se12	2.8106(17)	2.7945(13)	2.7927(6)	2.7758(12)
M4–Se11	2.8272(19)	2.8112(14)	2.8075(7)	2.7788(12)
M4–Se3	2.8440(17)	2.8230(13)	2.8219(7)	2.8067(12)
M4–Se6	2.8443(17)	2.8274(13)	2.8259(7)	2.8095(12)
M4–Se9	2.8550(17)	2.8287(13)	2.8297(7)	2.8199(12)
M4–Se12	2.8778(19)	2.8469(14)	2.8498(7)	2.8341(12)
RE5–Se1	2.7619(17)	2.7374(12)	2.7354(7)	2.7155(12)
RE5–Se2	2.7978(18)	2.7954(13)	2.7951(7)	2.7625(12)
RE5–Se7	2.8280(16)	2.8058(12)	2.8050(6)	2.7866(11)
RE5–Se5	2.8317(17)	2.8066(13)	2.8064(7)	2.7906(11)
RE5–Se4	2.8756(19)	2.8338(14)	2.8345(7)	2.8253(12)
RE5–Se10	2.9775(17)	2.9569(13)	2.9570(6)	2.9477(11)
RE6–Se8	2.7618(17)	2.7389(13)	2.7359(7)	2.7218(12)
RE6–Se2	2.8251(18)	2.7967(13)	2.7961(7)	2.7884(12)
RE6–Se12	2.8557(17)	2.8305(13)	2.8298(6)	2.8098(12)

RE6–Se3	2.8648(19)	2.8447(13)	2.8439(6)	2.8215(12)
RE6–Se5	2.8680(17)	2.8565(13)	2.8550(6)	2.8278(11)
RE6–Se10	2.8777(17)	2.8591(14)	2.8604(7)	2.8403(12)
RE7–Se8	2.7847(17)	2.7617(13)	2.7611(7)	2.7470(12)
RE7–Se7	2.8193(18)	2.8101(13)	2.8115(7)	2.7890(11)
RE7–Se11	2.8369(17)	2.8137(13)	2.8116(6)	2.7904(12)
RE7–Se9	2.8416(16)	2.8155(13)	2.8140(7)	2.7953(12)
RE7–Se5	2.8459(19)	2.8232(12)	2.8224(6)	2.8078(11)
RE7–Se4	2.8701(17)	2.8496(13)	2.8488(7)	2.8356(12)
RE8–Se1	2.7786(17)	2.7564(12)	2.7586(7)	2.7380(12)
RE8–Se4	2.8286(17)	2.8094(13)	2.8109(7)	2.7957(12)
RE8–Se7	2.8381(18)	2.8110(13)	2.8115(7)	2.7985(11)
RE8–Se5	2.8552(18)	2.8406(13)	2.8399(6)	2.8101(11)
RE8–Se7	2.8632(16)	2.8422(13)	2.8420(7)	2.8235(11)
RE8–Se2	2.9292(17)	2.9003(13)	2.8992(7)	2.8802(12)
Cd5–Se1 × 4	2.6608(16)	2.6518(12)	2.6501(7)	2.6433(12)
Cs–Se11	3.858(2)	3.8327(16)	3.8306(8)	3.8139(14)
Cs–Se1	3.915(2)	3.8806(15)	3.8806(8)	3.8552(15)
Cs–Se1	3.933(2)	3.8995(16)	3.8988(9)	3.8766(15)
Cs–Se4	3.940(2)	3.9003(15)	3.9027(9)	3.8922(15)
Cs–Se9	3.947(2)	3.9391(16)	3.9377(9)	3.9055(15)
Cs–Se12	3.964(2)	3.9493(16)	3.9489(8)	3.9099(15)
Cs–Se5	4.017(2)	3.9842(15)	3.9836(8)	3.9746(14)
Cs–Se8	4.107(2)	4.0565(16)	4.0555(9)	4.0057(16)
Cs–Se8	4.162(2)	4.1086(16)	4.1075(9)	4.0522(16)
Cs–Se2	4.193(2)	4.1582(16)	4.1549(8)	4.1285(15)
Cs–Se7	4.194(2)	4.1592(17)	4.1587(8)	4.1287(14)

Table S4. EDX results of $Cs_4[Tm_{26}Cd_7Se_{48}]$.

Crystal-1				Crystal-2			
Element	Weight%	Atomic%	Formula	Element	Weight%	Atomic%	Formula
Se L	40.53	56.66	46.49	Se L	40.36	56.50	48.70
Cd L	8.27	8.12	6.66	Cd L	8.41	8.27	7.13
Cs L	5.87	4.87	4	Cs L	5.58	4.64	4
Ho L	45.33	30.34	24.89	Ho L	45.65	30.59	26.37
Total	100.00			Total	100.00		
Crystal-3				Crystal-4			
Element	Weight%	Atomic%	Formula	Element	Weight%	Atomic%	Formula
Se L	40.88	57.05	56.64	Se L	40.09	56.27	44.84
Cd L	8.54	8.37	8.31	Cd L	7.98	7.87	6.27
Cs L	4.86	4.03	4	Cs L	6.02	5.02	4
Ho L	45.72	30.55	30.32	Ho L	45.91	30.85	24.58
Total	100.00			Total	100.00		
Crystal-5							
Element	Weight%	Atomic%	Formula				
Se L	40.31	56.45	47.78				
Cd L	8.37	8.23	6.97	Average formula:			
Cs L	5.68	4.73	4	$Cs_4Cd_{7.1\ (2)}\ Ho_{26.4\ (2)}\ Se_{48.9\ (5)}$			
Ho L	45.63	30.59	25.91				
Total	100.00						

References

[1] E. L. Simmons, Diffuse reflectance spectroscopy: a comparison of the theories. *Appl. Opt.,* 1975, **14**, 1380−1386.

[2] K. A. Borup, J. D. Boor, H. Wang, F. Drymiotis, F. Gascoin, X. Shi, L. D. Chen, M. I. Fedorov, E. Müller, B. B. Iversen and G. J. Snyder, Measuring thermoelectric transport properties of materials. *Energy Environ. Sci.*, 2015, **8**, 423–435.

[3] *CrystalClear* Version 1.3.5; Rigaku Corp.: Woodlands, TX, 1999.

[4] G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* 2008, 112–122.

[5] G. Kresse and J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B: Condens. Matter*, 1996, **54**, 11169–11186.

[6] J. P. Perdew and Y. Wang, Accurate and simple analytic representation of the electron-gas correlation energy. *Phys. Rev. B: Condens. Matter*, 1992, **45**, 13244–13249.

[7] G. Kresse and D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B: Condens. Matter*, 1999, **59**, 1758–1775.

[8] P. E. Blöchl, Projector augmented-wave method. *Phys. Rev. B: Condens. Matter*, 1994, **50**, 17953–17979.