Electronic Supplementary Information

A new type of novel salt-inclusion chalcogenides with ultralow thermal conductivity

Hong Chen,[a,b] Peng-Fei Liu,[c] Hua Lin,*[,a,b] and Xin-Tao Wu*[,a,b]

[a.] *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China*

[b.] *Fujian Science & Technology Innovation Laboratory for Optoelectronic Information of China, Fuzhou 350002, China*

[c.] *Spallation Neutron Source Science Center, Institute of High Energy Physics, Chinese Academy of Sciences, Dongguan 523803, China*

*E-mail: linhua@fjirsm.ac.cn and wxt@fjirsm.ac.cn.

Experimental Section

Materials and Instruments

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

= 3*nR*, 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.

Syntheses

$[Rb_6Cl][RE_{23}Mn_7Se_{44}]$ (RE = Ho–Yb). These compounds were obtained from a stoichiometric ratio of RbCl: RE: Mn: Se = 6:23:7:44. The reagents were mixed, sealed in an evacuated silica tube, and heated to 1223 K over a 100 h period, maintained there for 120 h, cooled to 573 K at 3 K/h, and then the furnace was turned off. The resultant materials were washed and dried with ethanol. A lot of good quality lump crystals were obtained. 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 Rb, RE, Se and Cl 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 773 K for 40 min under an axial compressive stress of 100MPa in vacuum) with a theoretical density of more than 90% were used for thermal conductivity measurements.

Crystal Structure Determinations

All data collections were performed on a Rigaku Saturn 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 $[Rb_6Cl][Ho_{23}Mn_7Se_{44}]$ for example, initially one Rb, one Cl, six Se, and five "Ho" atoms were easily located according to the bond distances and coordination environments. After refinement the *R* values were *R*1 =

10.30% and *wR*2 = 32.98%. With full occupancy, three of the "Ho" atoms (namely, Ho1, Ho2 and Ho3) exhibit a larger atomic displacement parameter, 0.020–0.038 Å^2, than those of other "Ho" atoms (namely, Ho4 and Ho5) (0.005–0.006 Å^2). Subsequently, a disorder model with Ho and Mn was used for these three sites, keeping the coordinates the same while freely varying the occupancies. All the atoms were refined anisotropically (*R*1 = 3.43%, *wR*2 = 7.47%). To satisfy the charge balance requirement, the final formula was $[Rb_6Cl][Ho_{23}Mn_7Se_{44}]$. This is agreement with the EDX data. 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.

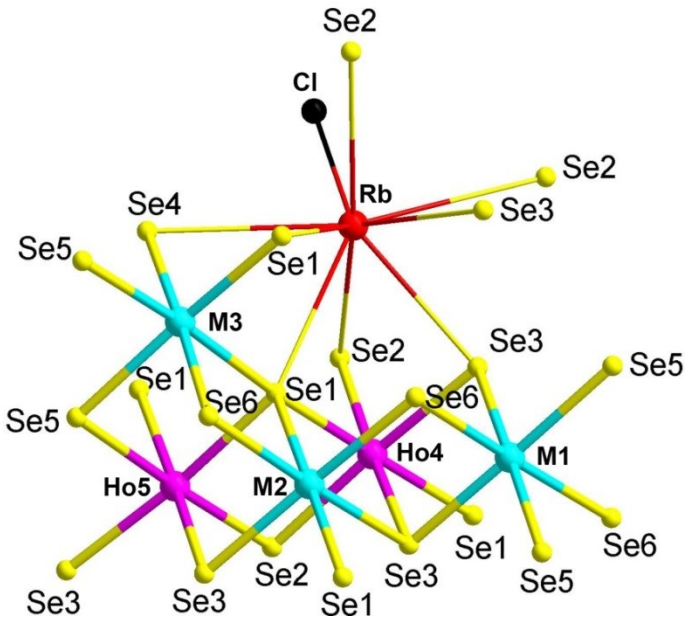

Fig. S1 Coordination geometry of $[Rb_6Cl][Ho_{23}Mn_7Se_{44}]$.

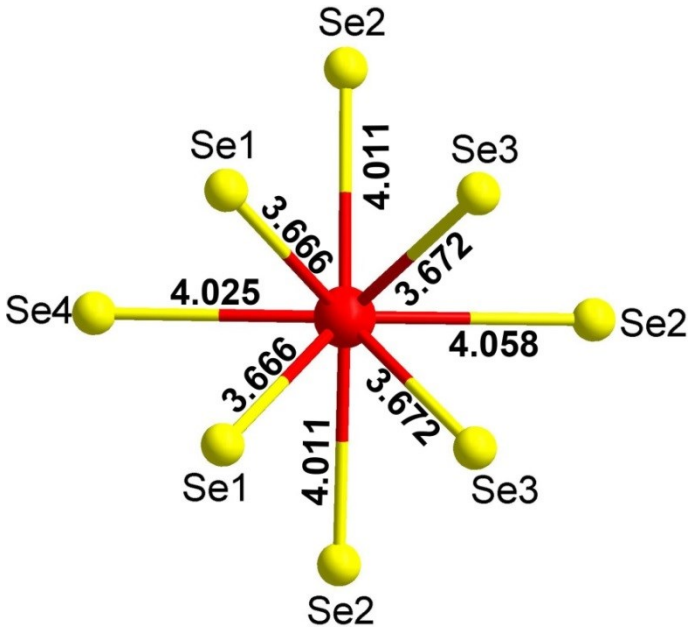

Fig. S2 Coordination geometry of Rb atom with distances marked.

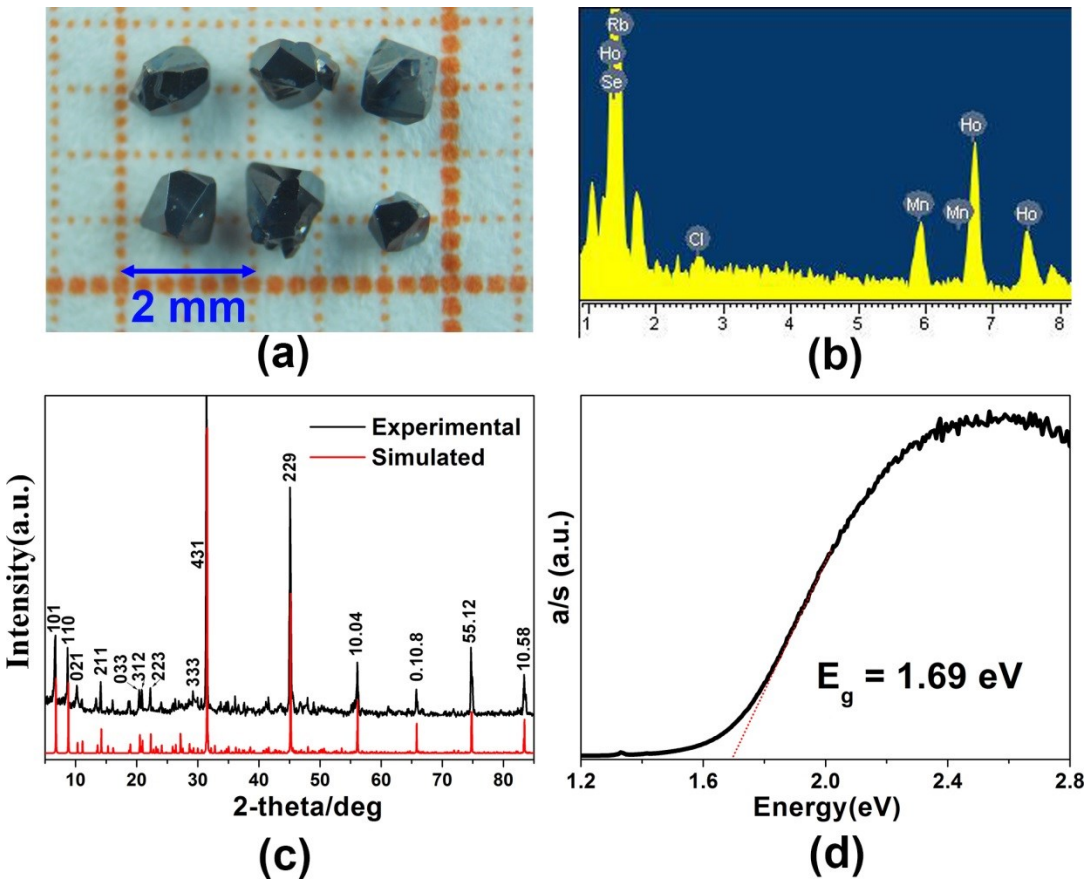

Fig. S3 Experimental results of $[Rb_6Cl][Ho_{23}Mn_7Se_{44}]$: (a) photograph of the crystals; (b) EDX spectrogram; (c) experimental and simulated powder XRD patterns; (d) UV-vis-NIR diffuse-reflectance spectrum.

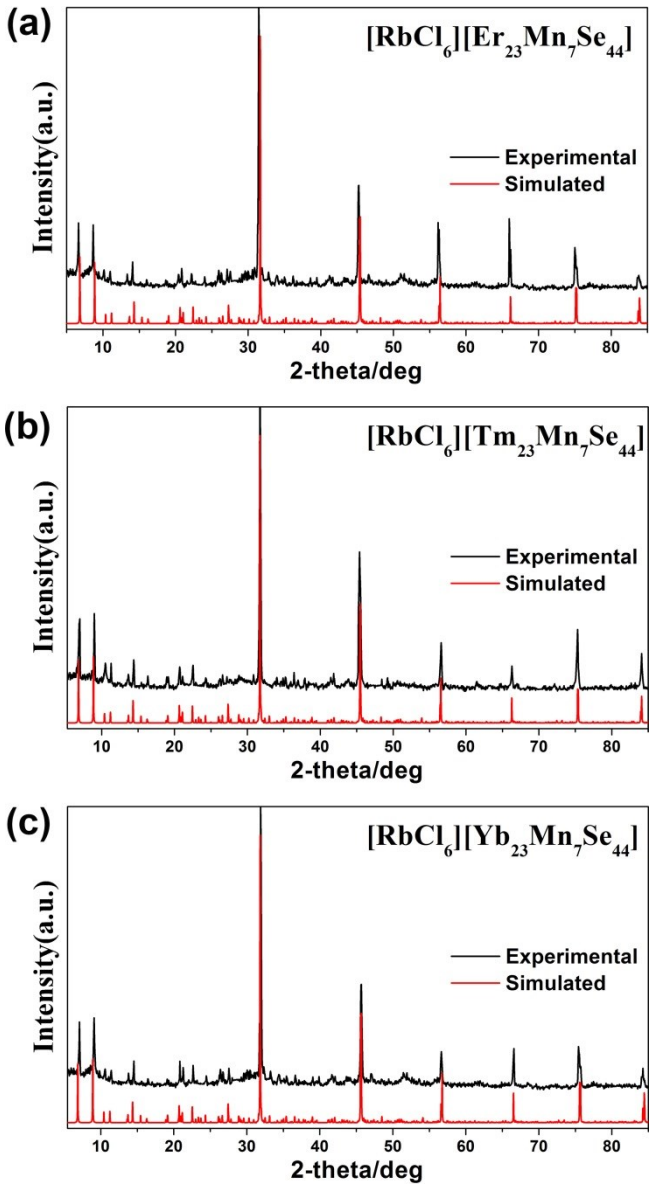

Fig. S4 Experimental (black) and simulated (red) powder XRD patterns of (a) $[Rb_6Cl][Er_{23}Mn_7Se_{44}]$ (b) $[Rb_6Cl][Tm_{23}Mn_7Se_{44}]$, and (c) $[Rb_6Cl][Yb_{23}Mn_7Se_{44}]$.

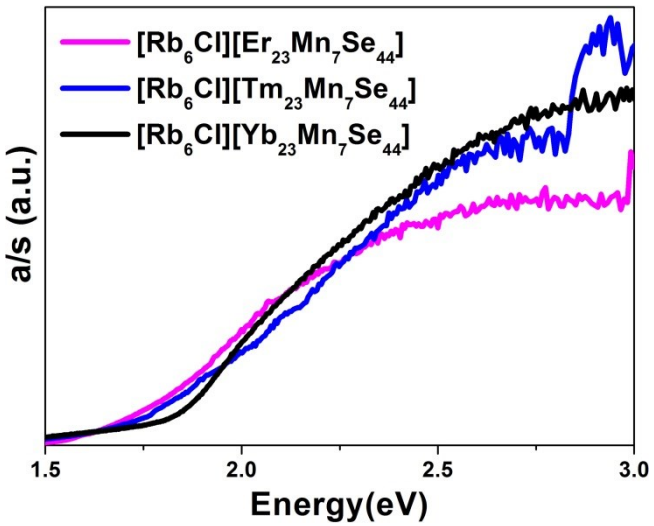

Fig. S5 UV-vis-NIR diffuse-reflectance spectra of $[Rb_6Cl][Yb_{23}Mn_7Se_{44}]$ (RE = Er, Tm and Yb).

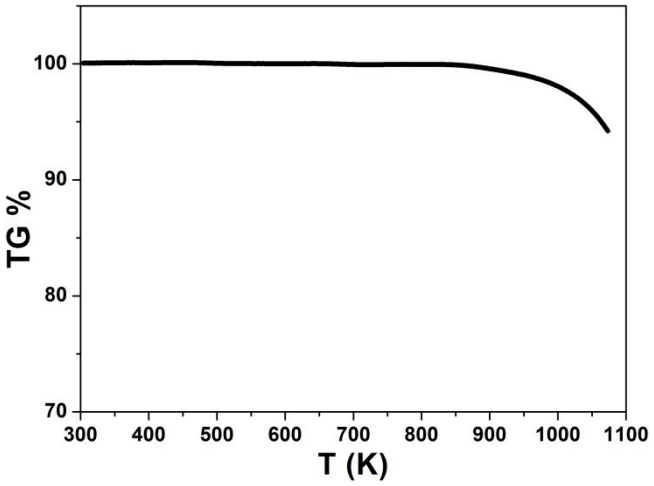

Fig. S6 The TG diagram of $[Rb_6Cl][Ho_{23}Mn_7Se_{44}]$.

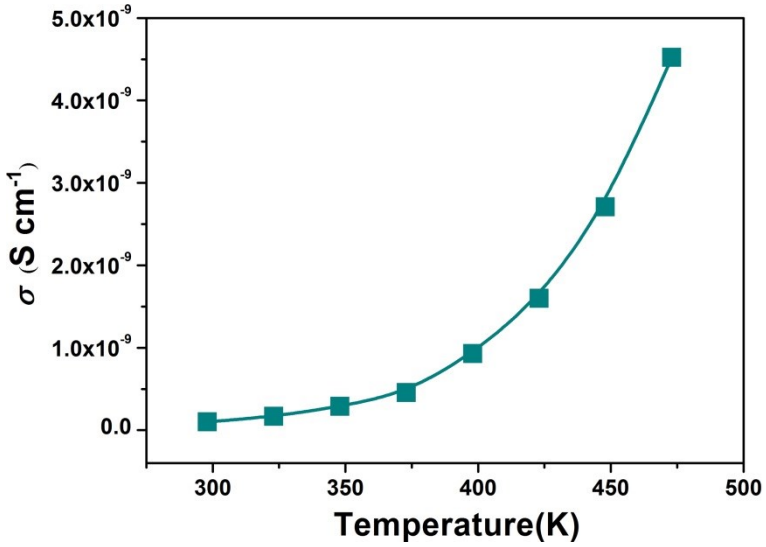

Fig. S7 Electrical conductivity (σ) as a function of temperature for $[Rb_6Cl][Ho_{23}Mn_7Se_{44}]$ using a K2500-5RSLP Variable Temperature Hall Measurement system.

Table S1 Crystallographic data and refinement details for $[Rb_6Cl][RE_{23}Mn_7Se_{44}]$ (RE = Ho–Yb).

Formula	$[Rb_6Cl][Ho_{23}Mn_7Se_{44}]$	$[Rb_6Cl][Er_{23}Mn_7Se_{44}]$	$[Rb_6Cl][Tm_{23}Mn_7Se_{44}]$	$[Rb_6Cl][Yb_{23}Mn_7Se_{44}]$
Fw	8200.47	8254.05	8292.55	8386.99
Temperature(K)		293(2)		
Crystal system		trigonal		
Space group		$R\bar{3}m$ (No. 166)		
a (Å)	20.0423(4)	19.9480(6)	19.914(2)	19.844(7)
b (Å)	20.0423(4)	19.9480(6)	19.914(2)	19.844(7)
c (Å)	19.6668(8)	19.595(2)	19.547(2)	19.496(9)
α (deg.)	90	90	90	90
β (deg.)	90	90	90	90
γ (deg.)	120	120	120	120
V (Å^3)	6841.6(3)	6752.6(5)	6713(2)	6649(5)
Z		3		
D_c (g cm^{-3})	5.971	6.089	6.154	6.284
μ (mm^{-1})	41.383	43.155	44.644	46.318
GOOF on F^2	1.022	1.067	1.088	1.097
R_1, wR_2 ($I > 2\sigma(I)$)	0.0334, 0.0718	0.0291, 0.0747	0.0431, 0.1012	0.0306, 0.0850
R_1, wR_2 (all data)	0.0366, 0.0734	0.0315, 0.0766	0.0481, 0.1045	0.0319, 0.0861
diff peak, hole (e. Å^{-3})	4.602, –4.009	4.908, –2.263	4.650, –5.032	3.235, –2.262

Table S2-1. Atomic coordinates and equivalent isotropic displacement parameters of $[Rb_6Cl][Ho_{23}Mn_7Se_{44}]$.

Atom	*Wyck.*	*x*	*y*	*z*	$U_{(eq)}$(Å^2)*	Occu.
M1 = Ho1/Mn1	18*f*	0.46676(4)	0.3333	0.3333	0.0115(2)	0.439(2)/0.561(2)
M2 = Ho2/Mn2	18*g*	0.3333	0.26658(3)	0.1667	0.0110(2)	0.700(2) /0.300(2)
M3 = Ho3/Mn3	18*h*	0.12990(3)	0.06495(2)	0.17196(3)	0.0108(2)	0.695(2) /0.305(2)
Ho4	18*f*	0.26437(2)	0.3333	0.3333	0.0087(2)	1.0
Ho5	18*h*	0.13672 (2)	0.27344(3)	0.16624(2)	0.0098(2)	1.0
Se1	36*i*	0.20175(4)	0.20232(4)	0.24731(4)	0.0124(2)	1.0
Se2	18*h*	0.13180(3)	0.26361(6)	0.41613(4)	0.0118(3)	1.0
Se3	36*i*	0.40028(4)	0.39692(4)	0.25272(3)	0.0119(2)	1.0
Se4	6*c*	0	0	0.25137(9)	0.0165(4)	1.0
Se5	18*h*	0.06734(3)	0.13468(6)	0.08393(5)	0.0127(3)	1.0
Se6	18*h*	0.40704(6)	0.20352(3)	0.24778(5)	0.0123(3)	1.0
Rb	18*h*	0.16142(7)	0.08071(4)	0.39827(7)	0.0394(3)	1.0
Cl	3*b*	0	0	0.5	0.037(2)	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 $[Rb_6Cl][Er_{23}Mn_7Se_{44}]$.

Atom	*Wyck.*	*x*	*y*	*z*	$U_{(eq)}$(Å^2)*	Occu.
M1 = Er1/Mn1	18*f*	0.46676(4)	0.3333	0.3333	0.0108(2)	0.439(2)/0.561(2)
M2 = Er2/Mn2	18*g*	0.3333	0.26700(3)	0.1667	0.0094(2)	0.700(2) /0.300(2)
M3 = Er3/Mn3	18*h*	0.13007(3)	0.06504(2)	0.17180(3)	0.0088(2)	0.695(2) /0.305(2)
Er4	18*f*	0.26424(2)	0.3333	0.3333	0.0083(2)	1.0
Er5	18*h*	0.13669(2)	0.27338(2)	0.16632(2)	0.0094(2)	1.0
Se1	36*i*	0.20176(4)	0.20230(4)	0.24746(4)	0.0092(2)	1.0
Se2	18*h*	0.13196(3)	0.26392(5)	0.41614(5)	0.0089(2)	1.0
Se3	36*i*	0.40037(4)	0.39734(4)	0.25257(3)	0.0088(2)	1.0
Se4	6*c*	0	0	0.25148(9)	0.0128(4)	1.0
Se5	18*h*	0.06739(3)	0.13477(5)	0.08409(5)	0.0086(2)	1.0
Se6	18*h*	0.40632(6)	0.20316(3)	0.24775(5)	0.0097(2)	1.0
Rb	18*h*	0.16104(8)	0.08052(4)	0.39834(7)	0.0385(3)	1.0
Cl	3*b*	0	0	0.5	0.028(2)	1.0

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

Table S2-3. Atomic coordinates and equivalent isotropic displacement parameters of $[Rb_6Cl][Tm_{23}Mn_7Se_{44}]$.

Atom	*Wyck.*	*x*	*y*	*z*	$U_{(eq)}$(Å^2)*	Occu.
M1 = Tm1/Mn1	18*f*	0.46665(5)	0.3333	0.3333	0.0120(3)	0.437(2)/0.563(2)
M2 = Tm2/Mn2	18*g*	0.3333	0.26706(4)	0.1667	0.0118(3)	0.729(2) /0.271(2)
M3 = Tm3/Mn3	18*h*	0.12987(4)	0.06493(2)	0.17181(4)	0.0112(3)	0.667(2) /0.333(2)
Tm4	18*f*	0.26417(3)	0.3333	0.3333	0.0112(2)	1.0
Tm5	18*h*	0.13673(2)	0.27345(3)	0.16628(3)	0.0111(2)	1.0
Se1	36*i*	0.20160(5)	0.20252(5)	0.24730(5)	0.0132(3)	1.0
Se2	18*h*	0.13183(4)	0.26366(8)	0.41611(7)	0.0125(4)	1.0
Se3	36*i*	0.40018(5)	0.39734(5)	0.25274(5)	0.0124(3)	1.0
Se4	6*c*	0	0	0.2518(2)	0.0172(6)	1.0
Se5	18*h*	0.06759(4)	0.13518(8)	0.08417(7)	0.0140(4)	1.0
Se6	18*h*	0.40661(8)	0.20330(4)	0.24742(7)	0.0125(4)	1.0
Rb	18*h*	0.1613(2)	0.08063(5)	0.39824(9)	0.0374(4)	1.0
Cl	3*b*	0	0	0.5	0.041(3)	1.0

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

Table S2-4. Atomic coordinates and equivalent isotropic displacement parameters of $[Rb_6Cl][Yb_{23}Mn_7Se_{44}]$.

Atom	*Wyck.*	*x*	*y*	*z*	$U_{(eq)}$(Å^2)*	Occu.
M1 = Yb1/Mn1	18*f*	0.46731(4)	0.3333	0.3333	0.0036(2)	0.385(2)/0.615(2)
M2 = Yb2/Mn2	18*g*	0.3333	0.26767(3)	0.1667	0.0038(2)	0.743(2) /0.257(2)
M3 = Yb3/Mn3	18*h*	0.13022(3)	0.06511(2)	0.17149(3)	0.0030(2)	0.706(2) /0.294(2)
Yb4	18*f*	0.26423(2)	0.3333	0.3333	0.0051(2)	1.0
Yb5	18*h*	0.13673(2)	0.27346(3)	0.16606(2)	0.0053(2)	1.0
Se1	36*i*	0.20143(4)	0.20245(4)	0.24763(4)	0.0045(2)	1.0
Se2	18*h*	0.13220(3)	0.26439(6)	0.41601(5)	0.0052(3)	1.0
Se3	36*i*	0.40012(4)	0.39764(4)	0.25263(4)	0.0050(2)	1.0
Se4	6*c*	0	0	0.2516(2)	0.0077(4)	1.0
Se5	18*h*	0.06765(3)	0.13530(6)	0.08471(5)	0.0046(3)	1.0
Se6	18*h*	0.40568(6)	0.20284(3)	0.24733(5)	0.0051(3)	1.0
Rb	18*h*	0.16067(8)	0.08034(4)	0.39887(7)	0.0339(3)	1.0
Cl	3*b*	0	0	0.5	0.025(2)	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 ($ClRb_6$) $[RE_{23}Mn_7Se_{44}]$ (RE = Ho–Yb).

	$[Rb_6Cl][Ho_{23}Mn_7Se_{44}]$	$[Rb_6Cl][Er_{23}Mn_7Se_{44}]$	$[Rb_6Cl][Tm_{23}Mn_7Se_{44}]$	$[Rb_6Cl][Yb_{23}Mn_7Se_{44}]$
M1–Se3 ×2	2.7588(8)	2.7530(8)	2.747(2)	2.754(2)
M1–Se6 ×2	2.8140(6)	2.8068(6)	2.8032(9)	2.801(2)
M1–Se5 ×2	2.8318(8)	2.8207(8)	2.815(2)	2.802(2)
M2–Se1 ×2	2.7808(7)	2.7700(7)	2.765(2)	2.762(2)
M2–Se3 ×2	2.8257(7)	2.8115(7)	2.807(2)	2.793(2)
M2–Se6 ×2	2.8620(7)	2.8495(7)	2.843(2)	2.835(2)
M3–Se4	2.7427(11)	2.737(2)	2.731(2)	2.729(2)
M3–Se1 ×2	2.8081(7)	2.7972(7)	2.795(2)	2.789(2)
M3–Se6	2.821(2)	2.814(2)	2.804(2)	2.798(2)
M3–Se5 ×2	2.8766(8)	2.8622(7)	2.857(2)	2.841(2)
RE4–Se2 ×2	2.8196(7)	2.8033(7)	2.799(2)	2.784(2)
RE4–Se1 ×2	2.8349(7)	2.8213(6)	2.814(2)	2.803(2)
RE4–Se3 ×2	2.8436(7)	2.8358(7)	2.827(2)	2.817(2)
RE5–Se2	2.795(2)	2.778(2)	2.776(2)	2.761(2)
RE5–Se3 ×2	2.8158(7)	2.8015(7)	2.800(2)	2.787(2)
RE5–Se1 ×2	2.8513(7)	2.8397(7)	2.828(2)	2.823(2)
RE5–Se5	2.902(2)	2.886(2)	2.875(2)	2.855(2)
Rb–Se1 ×2	3.666(2)	3.651(2)	3.646(2)	3.642(2)
Rb–Se2 ×2	4.011(8)	3.996(2)	3.986(8)	3.979(8)
Rb–Se3 ×2	3.672(2)	3.653(2)	3.641(2)	3.630(2)
Rb–Se2	4.059(2)	4.047(2)	4.036(2)	4.025(2)
Rb–Se4	4.024(2)	4.011(2)	3.998(2)	3.987(2)
Cl–Rb	3.443(2)	3.422(2)	3.420(2)	3.393(2)

Table S4 The EDX results of $[Rb_6Cl][Ho_{23}Mn_7Se_{44}]$.

Point-1				Point-2			
Element	Weight%	Atomic%	Formula	Element	Weight%	Atomic%	Formula
Cl K	0.63	1.79	1.49	Cl K	0.41	1.18	0.98
Mn K	4.52	8.31	6.89	Mn K	4.45	8.24	6.87
Se L	42.57	54.42	45.18	Se L	42.37	54.58	45.48
Rb L	6.12	7.23	6	Rb L	6.05	7.20	6
Ho L	46.16	28.25	23.45	Ho L	46.72	28.81	24.01
Total	100.00			Total	100.00		
Point-3				Point-4			
Element	Weight%	Atomic%	Formula	Element	Weight%	Atomic%	Formula
Cl K	0.57	1.63	1.32	Cl K	0.67	1.89	1.53
Mn K	4.68	8.61	7.01	Mn K	4.88	8.88	7.17
Se L	42.15	53.97	43.94	Se L	43.02	54.47	44.00
Rb L	6.23	7.37	6	Rb L	6.35	7.43	6
Ho L	46.37	28.42	23.14	Ho L	45.08	27.33	22.07
Total	100.00			Total	100.00		
Point-5							
Element	Weight%	Atomic%	Formula				
Cl K	0.81	2.29	1.96				
Mn K	5.04	9.21	7.88	Average formula:			
Se L	42.03	53.44	45.72	$Rb_6Ho_{23.3\,(7)}\,Mn_{7.2(4)}Se_{44.9\,(3)}\,Cl_{1.5\,(3)}$			
Rb L	5.97	7.01	6				
Ho L	46.08	28.05	24.01				
Total	100.00						

References

[1] E. L. Simmons, *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, *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.