Electronic supplementary information (ESI)

Syntheses, structural variants and characterization of $A_2CdSn_2S_6$ (A = Cs, Rb and K) compounds

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Table S1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameter ($Å^2 \times 10^3$) for $A_2CdSn_2S_6$ (A = Cs(**1**), Rb(**2**), K(**3-β**)) compounds.

Compound	Atom	Wyckoff site	*x*	*y*	*z*	* U_{eq}
$Cs_2CdSn_2S_6$(1)	Sn(1)	2*a*	6058(1)	7327(1)	6389(1)	14(1)
	Sn(2)	2*a*	7111(1)	52(1)	6735(1)	14(1)
	Cd(1)	2*a*	1616(1)	6062(1)	7755(1)	19(1)
	Cs(1)	2*a*	9526(1)	7629(1)	2731(1)	33(1)
	Cs(2)	2*a*	3400(1)	9222(1)	9787(1)	31(1)
	S(1)	2*a*	4456(2)	8888(1)	5156(3)	24(1)
	S(2)	2*a*	4659(3)	6546(1)	3263(3)	25(1)
	S(3)	2*a*	5181 (3)	6731(2)	8887(3)	24(1)
	S(4)	2*a*	9573(2)	7568 (1)	7522(3)	22(1)
	S(5)	2*a*	404 (3)	5162(2)	4568(3)	26(1)
	S(6)	2*a*	8568(3)	9701(1)	85(2)	20(1)
$Rb_2CdSn_2S_6$(2)	Sn(1)	2*a*	3906(1)	2654(1)	3699(1)	16(1)
	Sn(2)	2*a*	2881(1)	9934(1)	3114(1)	16(1)
	Cd(1)	2*a*	8357(1)	3960(1)	2374(1)	20(1)
	Rb(1)	2*a*	482(2)	2414(1)	7343(2)	42(1)
	Rb(2)	2*a*	6647(2)	799(1)	153(2)	37 (1)
	S(1)	2*a*	5625(4)	1081(2)	4873(4)	27(1)
	S(2)	2*a*	5422(4)	3400(2)	6923(4)	27(1)
	S(3)	2*a*	4653(4)	3335(2)	1163(4)	29(1)
	S(4)	2*a*	310(4)	2398(2)	2636(5)	28(1)
	S(5)	2*a*	9739(4)	4769(2)	5724(4)	28(1)
	S(6)	2*a*	1471(4)	363(2)	9737(4)	23(1)
$K_2CdSn_2S_6$(3-β)	Sn(1)	4*e*	2156(1)	2343(1)	63(1)	16(1)
	Sn(2)	4*e*	4205(1)	1139(1)	3085(1)	15(1)
	Cd(1)	4*e*	9237(1)	1184(1)	2302(1)	20(1)
	K(1)	4*e*	1603(2)	1094(1)	6561(1)	35(1)
	K(2)	4*e*	6812(1)	906(1)	8766(1)	31(1)
	S(1)	4*e*	5394(2)	1420(1)	5262(1)	24(1)
	S(2)	4*e*	8730(2)	2489(1)	7175(1)	22(1)
	S(3)	4*e*	669(2)	1068(1)	55(1)	22(1)
	S(4)	4*e*	4081(2)	2395(1)	8304(1)	28(1)
	S(5)	4*e*	6319(1)	409(1)	1869(1)	21(1)
	S(6)	4*e*	1639(1)	357(1)	3567(1)	21(1)

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

Table S2. Bond lengths (Å) and bond valence sums (BVS) for $A_2CdSn_2S_6$ (*A* = Cs(**1**), Rb(**2**), K(**3-β**)) compounds.

Bonds	**Bond lengths(Å)**		
	$Cs_2CdSn_2S_6$(1)	**$Rb_2CdSn_2S_6$(2)**	**$K_2CdSn_2S_6$(3-β)**
Sn(1)-S(1)	2.4544(18)	2.450(3)	2.4085(12)
Sn(1)-S(2)	2.4146(19)	2.413(3)	2.4417(12)
Sn(1)-S(3)	2.344(2)	2.340(3)	2.3423(12)
Sn(1)-S(4)	2.3521(15)	2.349(2)	2.3477(11)
BVS	4.115	4.150	4.181
Sn(2)-S(1)	2.4241(17)	2.420(3)	2.4131(12)
Sn(2)-S(2)	2.4287(19)	2.422(3)	2.4247(12)
Sn(2)-S(5)	2.3473(19)	2.338(2)	2.3658(11)
Sn(2)-S(6)	2.3633(17)	2.362(3)	2.3703(11)
BVS	4.108	4.170	4.071
Cd(1)-S(3)	2.5375(18)	2.535(3)	2.5763(12)
Cd(1)-S(4)	2.5168(19)	2.507(3)	2.5175(13)
Cd(1)-S(5)	2.5280(19)	2.526(3)	2.5509(12)
Cd(1)-S(6)	2.5201(19)	2.512(3)	2.5601(12)
BVS	2.198	2.232	2.054
A(1)-S(1)	3.7239(1)	3.643(3)	3.2271(15)
A(1)-S(2)	3.8527(0)	3.698(3)	3.1968(16)
A(1)-S(3)	3.5465(1)	3.388(3)	-
A(1)-S(4)	3.5753(1)	3.440(3)	3.2910(18)
A(1)-S(5)	3.6465(1)	3.408(3)	3.2758(17)
A(1)-S(6)	3.4024(1)	3.244(3)	3.2854(16)
A(1)-S(2)	-	-	-
A(1)-S(6)	-		3.3795(16)
A(2)-S(1)	3.8186(1)	3.700(3)	-
A(2)-S(2)	-	-	3.3782(16)
A(2)-S(3)	3.6496(1)	3.530(3)	3.1545(16)
A(2)-S(4)	3.4713(0)	3.313(3)	3.1851(17)
A(2)-S(5)	3.5861(1)	3.390(3)	3.2186(16)
A(2)-S(6)	3.6227(0)	3.575(3)	3.3749(16)
A(2)-S(6)	3.6889(1)	3.577(3)	-
A(2)-S(1)	3.8544(1)	-	-
A(2)-S(3)	3.8289(1)	-	-
A(2)-S(5)	-	-	3.3049(16)

Table S3. Dipole moment calculations for $Cs_2CdSn_2S_6$(**1**) and $Rb_2CdSn_2S_6$(**2**) compounds.

$Sn1S_4$ in $Cs_2CdSn_2S_6$			Cart. Coord.			Distance	Unit vector				Dipole moment			Atom	Positions		
Z	atom	Charges	*x*	*y*	*z*	Å	*x*	*y*	*z*	U.Vec	C_grav	C_charge	μ_debye				
50	Sn1	4.115142	2.488262	10.14978	4.407432									Sn1	0.6058	0.7327	0.6389
16	S3	-1.16058	1.131328	9.32392	6.130888	2.3439	-0.57892	-0.35234	0.735294	1	0.24242	0.27219	21.1157	S3	0.5181	0.6731	0.8887
16	S4	-1.13514	4.681563	10.48264	5.188996	2.3521	0.932487	0.141518	0.332284	1	0.24242	0.2719	20.9720	S4	0.9573	0.7568	0.7522
16	S2	-0.95871	2.394273	9.067658	2.251007	2.4146	-0.03893	-0.44816	-0.89308	1	0.24242	0.26985	19.9802	S2	0.4659	0.6546	0.3263
16	S1	-0.86071	1.697493	12.31207	3.556811	2.4545	-0.32217	0.880952	-0.34656	1	0.24242	0.26871	19.4356	S1	0.4456	0.8888	0.5156
				Cell Volume		685.95			Dipole Moment			Magnitude					
				Z		2			x	y	z						
									0.29246	3.69554	-2.0844	4.25294	debye				

$Sn2S_4$ in $Cs_2CdSn_2S_6$			Cart. Coord.			Distance	Unit vector				Dipole moment			Atom	Positions		
Z	atom	Charges	*x*	*y*	*z*	Å	*x*	*y*	*z*	U.Vec	C_grav	C_charge	μ_debye				
50	Sn2	4.10884	1.12297	6.99830	2.25266									Sn2	0.7111	0.0052	0.6735
16	S5	-1.1502	-1.0400	7.14984	3.15150	2.3472	-0.9215	0.06456	0.38294	1	0.24242	0.27204	21.0403	S5	0.0404	0.5162	0.4568
16	S6	-1.1012	1.05248	6.51196	-0.0589	2.3633	-0.0298	-0.2057	-0.9781	1	0.24242	0.27148	20.7637	S6	0.8568	0.9701	0.0085
16	S1	-0.9344	2.56885	5.38607	3.34198	2.4241	0.59645	-0.6650	0.44937	1	0.24242	0.26954	19.8268	S1	0.4456	0.8888	0.5156
16	S2	-0.9228	2.39427	9.06765	2.25100	2.4287	0.52344	0.85204	-0.0006	1	0.24242	0.26941	19.7625	S2	0.4659	0.6546	0.3263
				Cell Volume		685.95			Dipole Moment			Magnitude					
				Z		2			x	y	z						
									2.16148	0.73734	-3.3559	4.0593	debye				

$Cd1S_4$ in $Cs_2CdSn_2S_6$			Cart. Coord.			Distance	Unit vector				Dipole moment			Atom	Positions		
Z	atom	Charges	*x*	*y*		Å	*x*	*y*	*z*	U.Vec	C_grav	C_charge	μ_debye				
48	Cd1	2.19828	6.08026	8.39652	5.34994					1				Cd1	0.1616	0.6062	0.7755
16	S4	-0.5627	4.68156	10.4826	5.18899	2.5167	-0.5557	0.82890	-0.0639	1	0.24242	0.26558	17.4451	S4	0.9573	0.7568	0.7522
16	S6	-0.5576	5.31883	6.51196	6.83987	2.5201	-0.3021	-0.7478	0.59121	1	0.24242	0.26552	17.4215	S6	0.8568	0.9701	0.0085
16	S5	-0.5458	6.13809	7.14984	3.15150	2.528	0.02287	-0.4931	-0.8696	1	0.24242	0.26538	17.3678	S5	0.0404	0.5162	0.4568
16	S3	-0.5320	8.30942	9.32392	6.13088	2.5375	0.87848	0.36547	0.30776	1	0.24242	0.26521	17.3054	S3	0.5181	0.6731	0.8887
				Cell Volume		685.95			Dipole Moment			Magnitude					
				Z		2			x	y	z						
									0.64073	-0.8078	-0.5934	1.18971	debye				

Vector Analysis of Dipole Moments

Center of Charge and Gravity: C_grav and C_charge = Center of mass for protons and electrons, respectively. Units are in Å and the value lies on the vector between Sn-S/ Cd-S

R (total distance)

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<------------>X<----------------------> X = Center of mass

a b

From the following two equations:

a + b = R ia = ib (at center of mass) i,i = masses (or charges) of i and i

then by solving for b in eqn #1, and substituting... a + (i/j)a = R a (1 + i/j) = R a = R / (1 + i/j) u_Debye is given in units of 10^{-10} esu*cm, or Debye Units μ_debye = neR

Table S3. Dipole moment calculations for $Cs_2CdSn_2S_6$(**1**) and $Rb_2CdSn_2S_6$(**2**) compounds (contd.).

$Sn1S_4$ in $Rb_2CdSn_2S_6$			Cart. Coord.			Distance	Unit vector				Dipole moment			Atom	Positions		
Z	atom	Charges	*x*	*y*	*z*	Å	*x*	*y*	*z*	U.Vec	C_grav	C_charge	μ_debye				
50	Sn1	4.150784	1.635932	3.635226	2.505671									Sn1	0.3906	0.2654	0.3699
16	S3	-1.17383	2.921466	4.56845	0.787927	2.3397	0.549444	0.398865	-0.73417	1	0.24242	0.272501	21.2876	S3	0.4653	0.3335	0.1163
16	S2	-1.14407	1.734507	4.657079	4.689561	2.3492	0.041961	0.434979	0.929631	1	0.24242	0.272157	21.1199	S2	0.5422	0.3400	0.6923
16	S4	-0.96235	-0.57253	3.285037	1.785841	2.4132	-0.91516	-0.14511	-0.29829	1	0.24242	0.270051	20.1006	S4	0.0310	0.2398	0.2636
16	S1	-0.87053	2.492073	1.481493	3.300596	2.4503	0.349403	-0.87897	0.324419	1	0.24242	0.268983	19.5915	S1	0.5422	0.1081	0.4873
				Cell Volume		652.24			Dipole Moment			Magnitude					
				Z		2			x	y	z						
									1.03263	-2.4595	4.36499	5.11557	debye				
$Sn2S_4$ in $Rb_2CdSn_2S_6$			Cart. Coord.			Distance	Unit vector				Dipole moment			Atom	Positions		
Z	atom	Charges	*x*	*y*	*z*	Å	*x*	*y*	*z*	U.Vec	C_grav	C_charge	μ_debye				
50	Sn2	4.170486	1.090844	13.60754	2.109425									Sn2	0.2881	0.9934	0.3114
16	S5	-1.17923	-1.09915	13.38248	2.896336	2.338	-0.9367	-0.09626	0.336574	1	0.24242	0.272648	21.37178	S5	0.9739	0.4769	0.5724
16	S6	-1.10517	1.112862	14.1963	-0.17795	2.362	0.009322	0.249264	-0.9684	1	0.24242	0.271792	20.95503	S6	0.1471	0.0363	0.9737
16	S1	-0.94533	2.492214	15.17999	3.300596	2.4198	0.579126	0.649827	0.49226	1	0.24242	0.269938	20.06138	S1	0.5625	0.1081	0.4873
16	S2	-0.94075	2.294561	11.50633	2.084227	2.4216	0.497075	-0.8677	-0.01041	1	0.24242	0.269885	20.0359	S2	0.5422	0.3400	0.6923
				Cell Volume		652.24			Dipole Moment			Magnitude					
				Z		2			x	y	z						
									1.75387	-1.1826	-3.4328	4.03226	debye				
$Cd1S_4$ in $Rb_2CdSn_2S_6$			Cart. Coord.			Distance	Unit vector				Dipole moment			Atom	Positions		
Z	atom	Charges	*x*	*y*		Å	*x*	*y*	*z*	U.Vec	C_grav	C_charge	μ_debye				
48	Cd1	2.232449	5.161976	5.424524	1.608002					1				Cd1	0.8357	0.3960	0.2374
16	S3	-0.53577	2.921395	4.568587	0.787927	2.5349	-0.88389	-0.33766	-0.32351	1	0.24242	0.265407	17.42307	S3	0.4653	0.3335	0.1163
16	S4	-0.57804	6.456425	3.285174	1.785841	2.5068	0.516375	-0.85342	0.070943	1	0.24242	0.265906	17.61529	S4	0.310	0.2398	0.2636
16	S5	-0.54866	5.128339	6.533376	3.877424	2.5261	-0.01332	0.438958	0.89839	1	0.24242	0.26556	17.48104	S5	0.9739	0.4769	0.5724
16	S6	-0.56998	5.916238	7.347053	0.177947	2.512	0.300264	0.765338	-0.56929	1	0.24242	0.265811	17.57815	S6	0.1471	0.363	0.9737
				Cell Volume		652.24			Dipole Moment			Magnitude					
				Z		2			x	y	z						
									-1.25873	0.21036	1.31080	1.829445	debye				

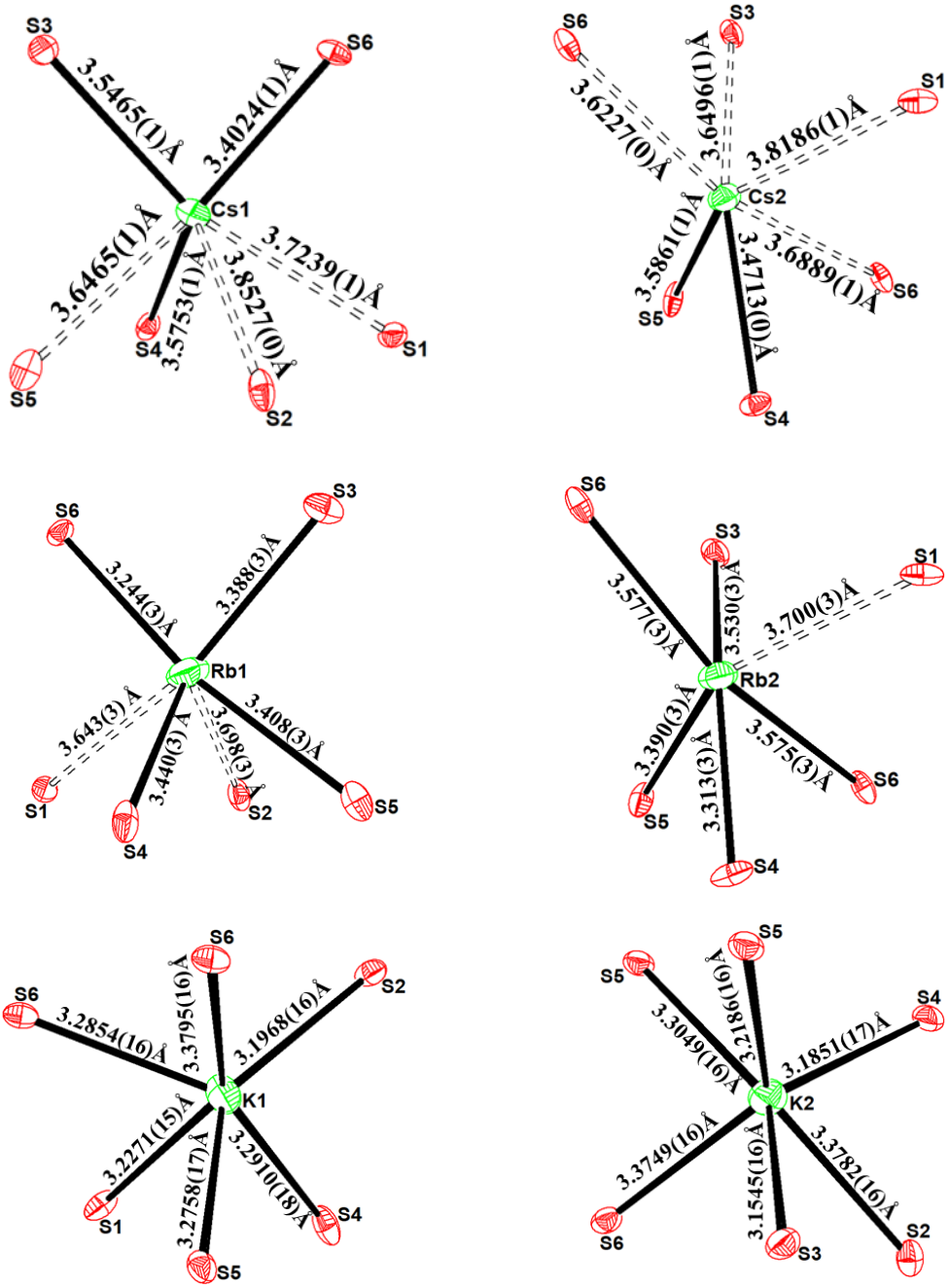

Figure S1. ORTEP diagrams of coordinations of Cs^+ (top), Rb^+ (middle) and K^+ (bottom) ions in $A_2CdSn_2S_6$ (A = Cs(**1**), Rb(**2**) and K(**3-β**)) compounds.

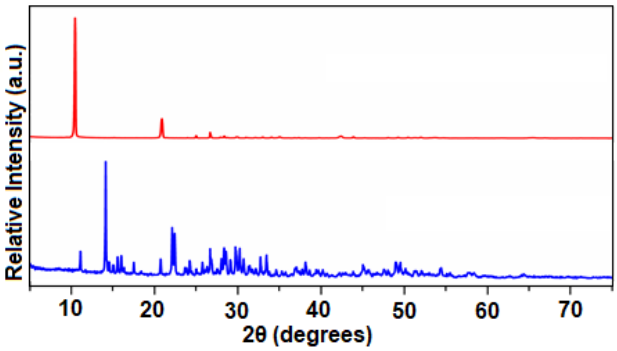

Figure S2. Powder XRD patterns of (bottom) $K_2CdSn_2S_6$(**3-β**) and (top) its thermally transformed product, $K_2CdSn_2S_6$(**3-α**).

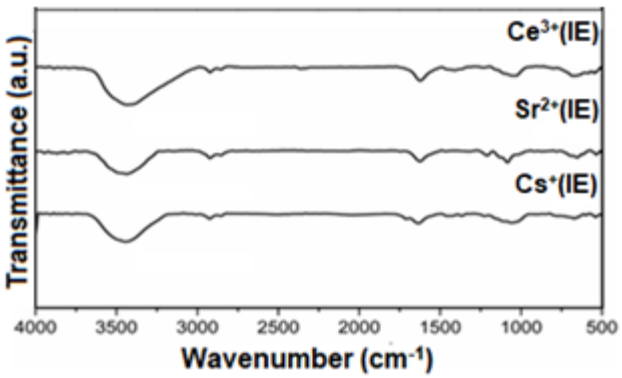

Figure S3. FT-IR spectra of ion-exchanged products, $(H_3O)Cs[CdSn_2S_6]$, $Sr[CdSn_2S_6]$ and $Ce_{⅔}[CdSn_2S_6]$.

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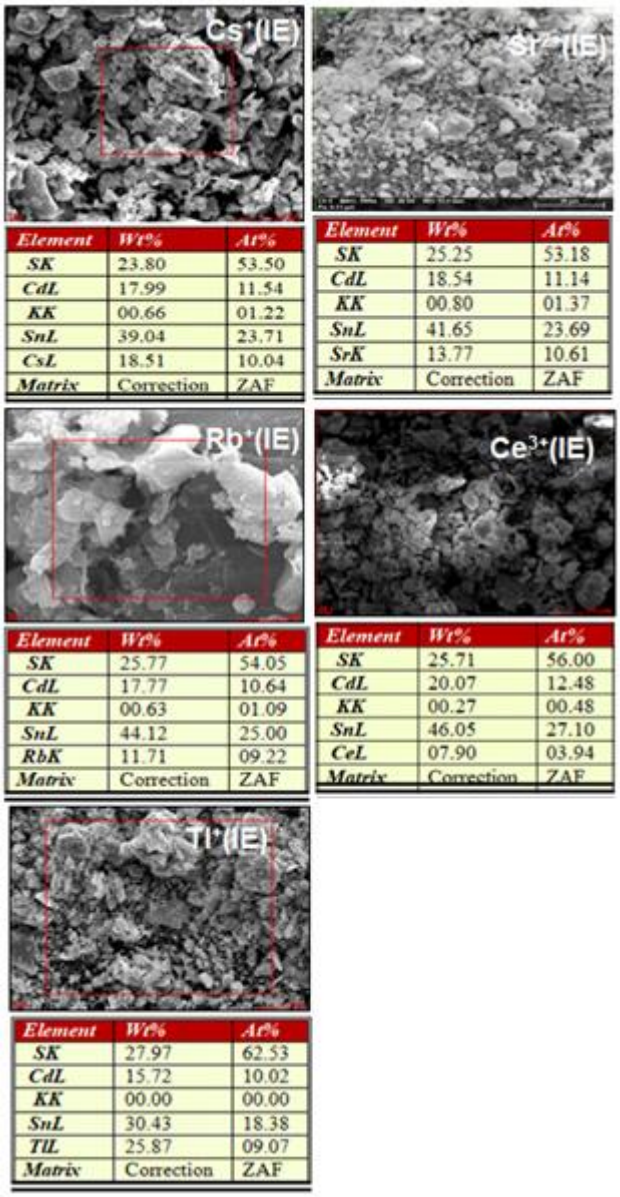

Figure S4. SEM and EDAX analysis ion-exchanged products, $(H_3O)A[CdSn_2S_6]$ (A = Rb, Cs, Tl), $Sr[CdSn_2S_6]$ and $Ce_{⅔}[CdSn_2S_6]$.