Indirect-to direct bandgap transition in CsRESiS4 (RE = Sc, Y, Lanthanides) through intrinsic charge-transfer- transitions (CTT) behaviour

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1 The structural properties of $CsRESiS_4$

Table S1. Calculated lattice constant(Å), volume (Å^3) and Average bond length RE-S (Å) for $CsRESiS_4$ using the PBE with the 4*f* in the core.

Materials	a (Å)	b (Å)	c (Å)	V (Å^3)	RE-S (Å)
$CsScSiS_4$	17.832	6.717	6.189	741.3	2.67
$CsYSiS_4$	17.998	6.742	6.402	776.9	2.81
$CsLaSiS_4$	18.239	6.774	6.642	820.6	2.96
$CsCeSiS_4$	18.255	6.780	6.609	818.0	2.96
$CsPrSiS_4$	18.186	6.769	6.573	809.2	2.93
$CsNdSiS_4$	18.165	6.761	6.540	803.3	2.91
$CsPmSiS_4$	18.122	6.759	6.502	796.3	2.89
$CsSmSiS_4$	18.097	6.750	6.485	792.2	2.87
$CsEuSiS_4$	18.057	6.742	6.467	787.3	2.85
$CsGdSiS_4$	18.026	6.747	6.439	783.1	2.84
$CsTbSiS_4$	18.023	6.737	6.419	779.4	2.82
$CsDySiS_4$	18.011	6.739	6.396	776.2	2.81
$CsHoSiS_4$	17.995	6.740	6.378	773.6	2.80
$CsErSiS_4$	17.972	6.743	6.360	770.7	2.79
$CsTmSiS_4$	17.950	6.734	6.348	767.3	2.78
$CsYbSiS_4$	17.940	6.735	6.330	764.8	2.76
$CsLuSiS_4$	17.916	6.735	6.316	762.1	2.75

Table S2. Calculated lattice constant(Å), volume (Å^3) and Average bond length RE-S (Å) for $CsRESiS_4$ using the PBE with the 4*f* in the valence.

Materials	a (Å)	b (Å)	c (Å)	V (Å^3)	RE-S (Å)
$CsLaSiS_4$	18.239	6.772	6.634	819.3	2.96
$CsCeSiS_4$	18.181	6.751	6.560	805.2	2.92
$CsPrSiS_4$	18.140	6.737	6.536	798.8	2.90
$CsNdSiS_4$	18.113	6.732	6.546	798.2	2.90
$CsPmSiS_4$	18.100	6.721	6.551	797.0	2.89
$CsSmSiS_4$	18.133	6.727	6.554	799.4	2.90
$CsEuSiS_4$	18.272	6.641	6.652	807.2	2.93
$CsGdSiS_4$	18.043	6.748	6.448	785.0	2.84
$CsTbSiS_4$	18.035	6.737	6.430	781.4	2.83
$CsDySiS_4$	18.000	6.729	6.393	774.2	2.80
$CsHoSiS_4$	17.963	6.723	6.414	774.5	2.81
$CsErSiS_4$	17.895	6.691	6.365	762.1	2.79
$CsTmSiS_4$	17.957	6.651	6.328	755.7	2.82
$CsLuSiS_4$	17.934	6.749	6.332	766.4	2.76

Table S3. Calculated lattice constant(Å), volume (Å^3) and Average bond length RE-S (Å) for $CsRESiS_4$ (RE=Ce-Lu) using the PBE+*U* (*U*=3) with the 4*f* in the valence.

Materials	a (Å)	b (Å)	c (Å)	V (Å^3)	RE-S (Å)
$CsCeSiS_4$	18.193	6.750	6.603	810.8	2.94
$CsPrSiS_4$	18.168	6.743	6.553	802.8	2.92
$CsNdSiS_4$	18.141	6.742	6.549	801.0	2.90
$CsPmSiS_4$	18.067	6.737	6.567	799.4	2.89
$CsSmSiS_4$	18.266	6.629	6.587	797.6	2.92
$CsEuSiS_4$	18.656	6.297	6.834	802.9	2.98
$CsGdSiS_4$	18.052	6.749	6.451	785.9	2.84
$CsTbSiS_4$	18.021	6.740	6.431	781.1	2.83
$CsDySiS_4$	18.007	6.744	6.409	778.3	2.81
$CsErSiS_4$	17.960	6.773	6.400	778.6	2.80
$CsTmSiS_4$	17.886	6.704	6.303	755.8	2.81
$CsLuSiS_4$	17.933	6.741	6.315	763.4	2.76

Table S4. Calculated lattice constant(Å), volume (Å^3) and Average bond length RE-S (Å) for $CsRESiS_4$ (RE = Sm-Dy, Er, Tm, Lu) using the PBE+*U* (*U*=7) with the 4*f* in the valence.

Materials	a (Å)	b (Å)	c (Å)	V (Å^3)	RE-S (Å)
$CsCeSiS_4$	18.219	6.781	6.589	813.9	2.95
$CsPrSiS_4$	18.186	6.763	6.567	807.6	2.92
$CsNdSiS_4$	18.147	6.762	6.552	803.9	2.91
$CsPmSiS_4$	18.101	6.747	6.541	798.8	2.89
$CsSmSiS_4$	18.117	6.727	6.512	793.6	2.88
$CsEuSiS_4$	19.447	5.988	7.107	827.6	3.10
$CsGdSiS_4$	18.041	6.749	6.442	784.4	2.84
$CsTbSiS_4$	18.023	6.735	6.393	776.1	2.81
$CsDySiS_4$	17.991	6.727	6.377	771.7	2.80
$CsErSiS_4$	17.968	6.731	6.373	770.8	2.79
$CsTmSiS_4$	17.936	6.736	6.329	764.6	2.77
$CsLuSiS_4$	17.892	6.727	6.275	755.2	2.73

Tables S5. Calculated values of the magnetic moments of the RE elements in the $CsRESiS_4$ compounds under the PBE+*U* conditions (*U*=3, 7 eV)

Materials	*U*=3	*U*=7
$CsScSiS_4$	0	-
$CsYSiS_4$	0	-
$CsLaSiS_4$	0	-
$CsCeSiS_4$	0.984	-
$CsPrSiS_4$	2.005	-
$CsNdSiS_4$	3.002	-
$CsPmSiS_4$	4.129	-
$CsSmSiS_4$	5.236	-
$CsEuSiS_4$	6.597	6.919
$CsGdSiS_4$	6.982	7.054
$CsTbSiS_4$	5.948	6.061

$CsDySiS_4$	4.935	5.046
$CsHoSiS_4$	3.903	4.027
$CsErSiS_4$	1.072	2.982
$CsTmSiS_4$	1.625	1.971
$CsLuSiS_4$	0	0

Table S6. Calculated bandgap values (eV) of $CsRESiS_4$ obtained using PBE for $CsScSiS_4$ and $CsYSiS_4$, PBE+*U* (*U* = 3) for $CsRESiS_4$ (RE = La–Lu), and HSE for $CsRESiS_4$ (RE = La–Gd).

Materials	PBE	HSE	Expt.
$CsScSiS_4$	1.93	-	-
$CsYSiS_4$	2.59	-	3.80[1]
$CsLaSiS_4$	2.68	3.61	3.64[2]
$CsCeSiS_4$	2.49	2.93	-
$CsPrSiS_4$	1.87	2.86	-
$CsNdSiS_4$	1.39	2.45	-
$CsPmSiS_4$	0.44	1.88	-
$CsSmSiS_4$	0	0.64	-
$CsEuSiS_4$	2.18	0.81	-
$CsGdSiS_4$	2.47	3.26	-

Tables S7. Elastic constants and deformation potential of $CsXSiS_4$ compound.

Materials	C_{xx}	C_{yy}	C_{zz}	E_{xx}	E_{yy}	E_{zz}
$CsLaSiS_4$	33.50	44.08	37.48	6.17	8.71	9.13
$CsCeSiS_4$	34.17	45.90	35.99	5.26	8.56	6.12
$CsPrSiS_4$	35.22	45.52	40.65	6.15	10.04	6.63
$CsNdSiS_4$	35.01	34.28	41.09	5.58	7.62	6.30
$CsPmSiS_4$	34.72	43.30	31.06	4.73	8.61	7.76
$CsSmSiS_4$	34.19	30.46	38.30	4.07	13.54	8.20
$CsEuSiS_4$	30.10	22.14	37.33	3.90	19.71	5.00
$CsGdSiS_4$	44.91	61.56	58.55	4.91	10.67	8.76

2 The Band Structure, Projected Density of States and absorption coefficient for $CsRESiS_4$

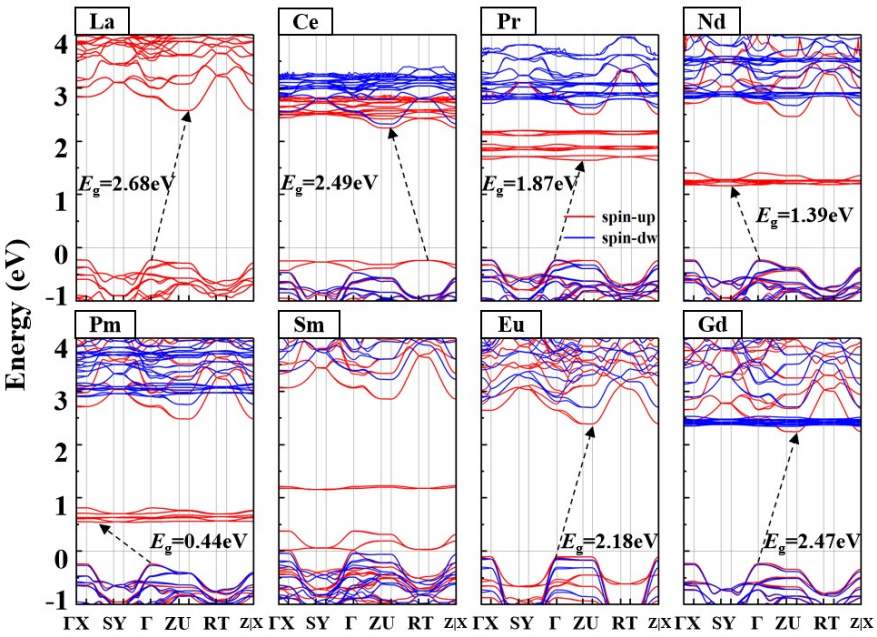

Fig. S1 Band structures calculated using PBE+U (U=3 eV) for $CsRESiS_4$ (RE = La–Gd).

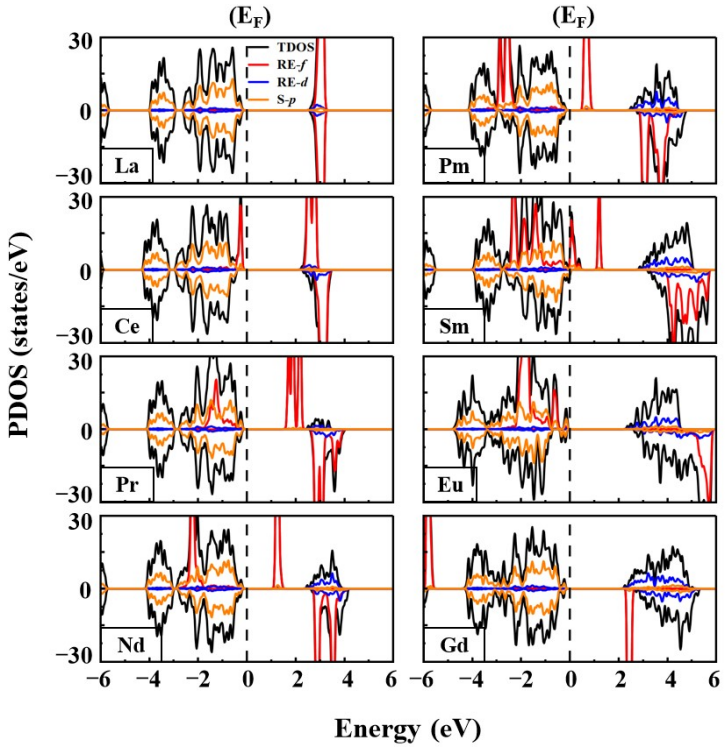

Fig. S2 Projected DOS calculated using PBE+U (U = 3 eV) for $CsRESiS_4$ (RE = La–Gd).

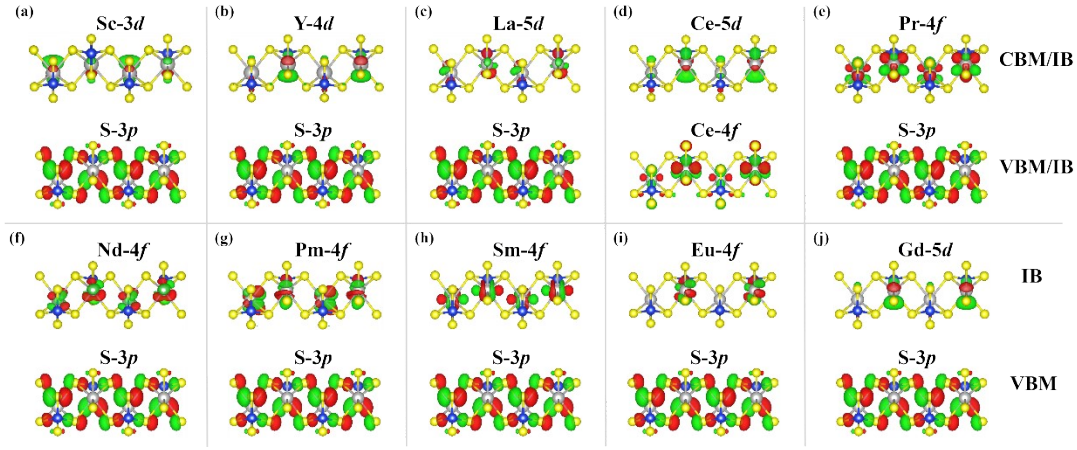

Fig. S3 Partial charge densities of the CBM, VBM and IB for $CsScSiS_4$ and $CsYSiS_4$ calculated using PBE, and for CsRESiS4 (RE = La–Gd) calculated using HSE.

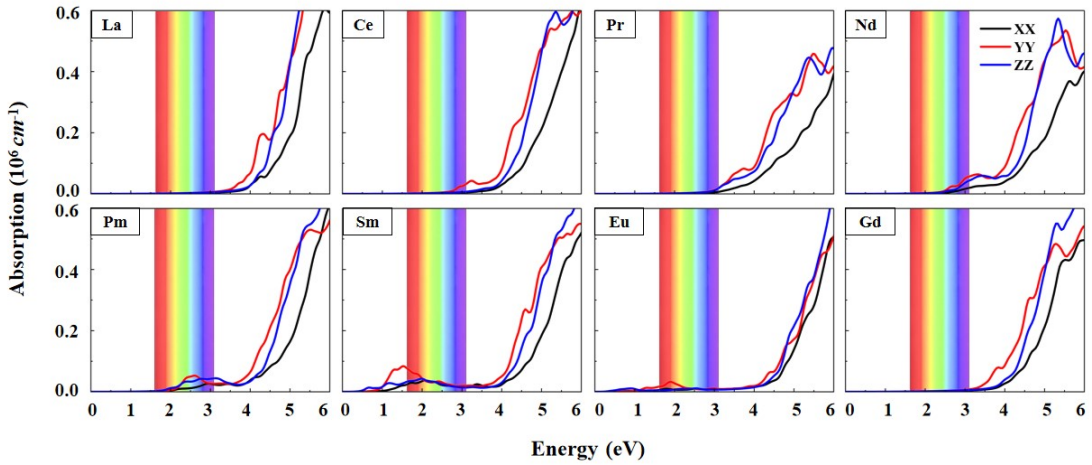

Fig. S4 Optical absorption spectra of $CsRESiS_4$ (RE = La-Gd) for XX (black), YY (red), and ZZ (blue) polarized light. Colored bar: visible light range for reference.

3 The elastic constant and deformation potential energy for $CsRESiS_4$

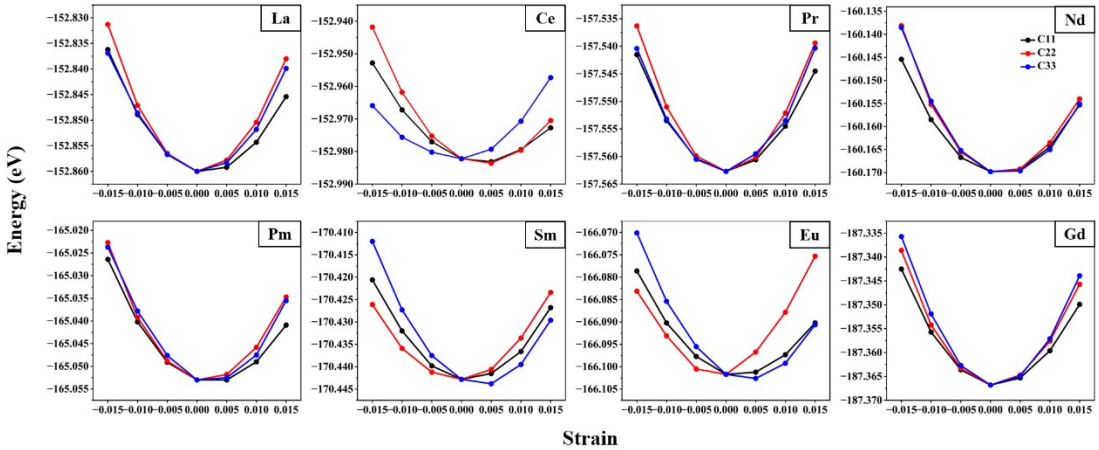

Fig. S5 The total energy of $CsRESiS_4$ (RE = La-Gd) is fitted by a parabola with respect to deformation, which determines the elastic constants.

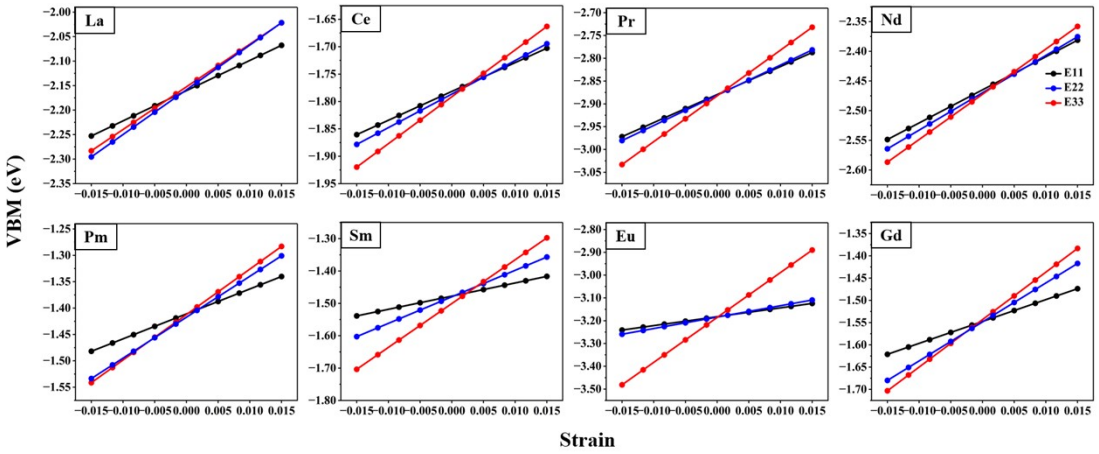

Fig. S6 The valence band edge positions of $CsRESiS_4$ (RE = La-Gd) under three different strain directions are shown. The solid lines represent the linear fits, which determine the deformation potential.

1 Tarasenko, M. S., Duritsyn, R. V., Potapov, D. A., Kuratieva, N. V., Ryadun, A. A., & Naumov, N. G. (2022). Double yttrium thiosilicates A $YSiS_4$ (A= Rb, Cs): synthesis, structure, optical properties. *Journal of Structural Chemistry*, *63*(12), 1988-1996.

2 Yang, L.; Li, Z.; He, L.; Sun, J.; Wang, J.; Wang, Y.; Li, M.; Zhu, Z.; Dai, X.; Hu, S.-X.; Zhai, F.; Yang, Q.; Tao, Y.; Chai, Z.; Wang, S.; Wang, Y. Emergence of a Lanthanide Chalcogenide as an Ideal Scintillator for a Flexible X-ray Detector, *Angew. Chem. Int. Ed*., 2023, 62, e202306465.