Supporting Information for

Infrared Nonlinear Optical Sulfide $CsCd_4In_5S_{12}$ exhibiting Large Second Harmonic Generation Response

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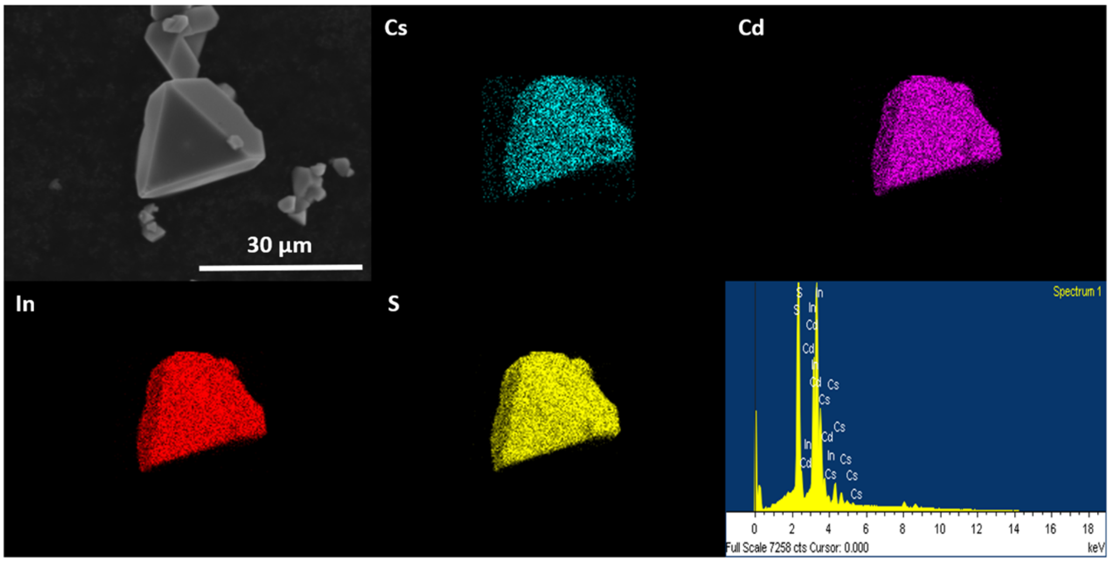

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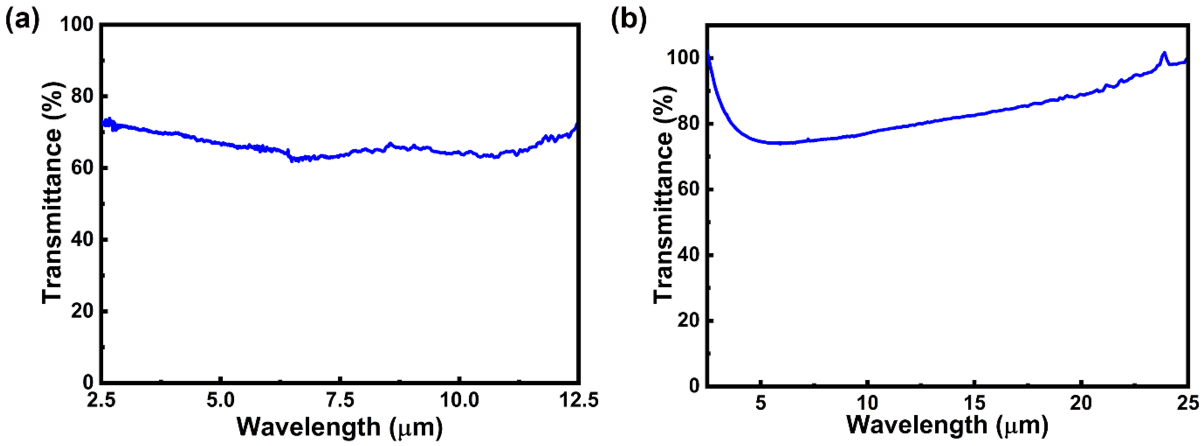

Figure S2. IR spectrum of $CsCd_4In_5S_{12}$ measured with a single crystal (a) and powder sample (b)

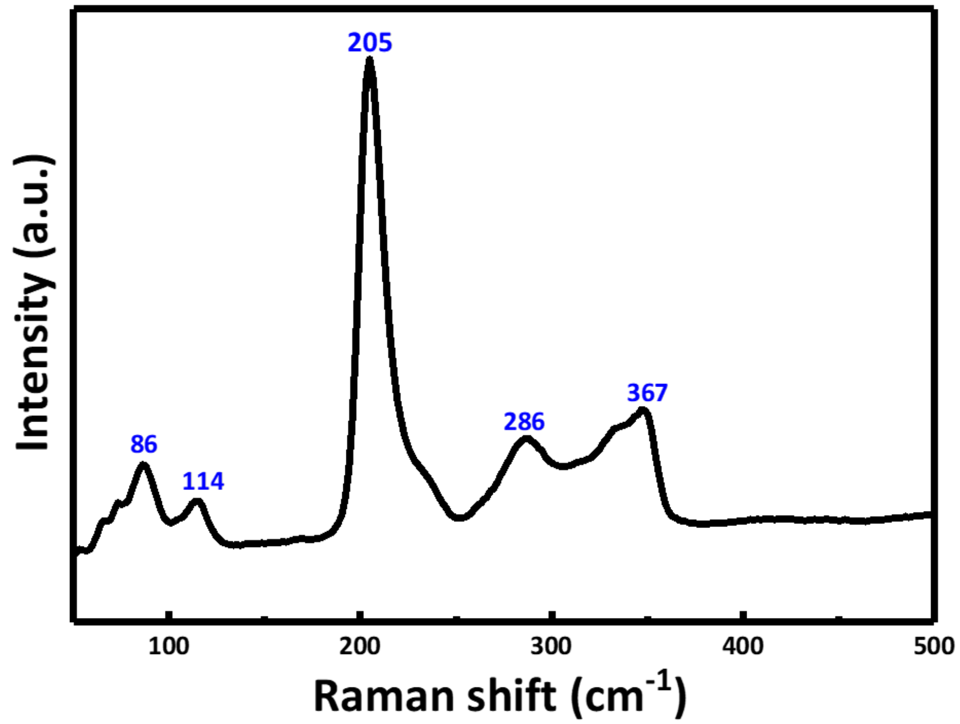

Figure S3. Raman spectrum of $CsCd_4In_5S_{12}$.

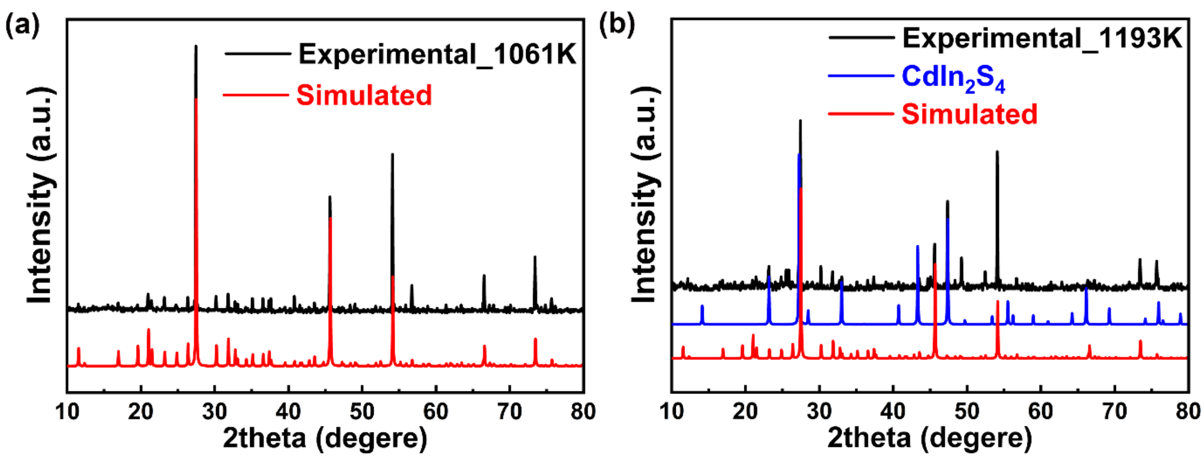

Figure S4. PXRD of $CsCd_4In_5S_{12}$ after being heated at 1061 K (a) and 1193 K (b)

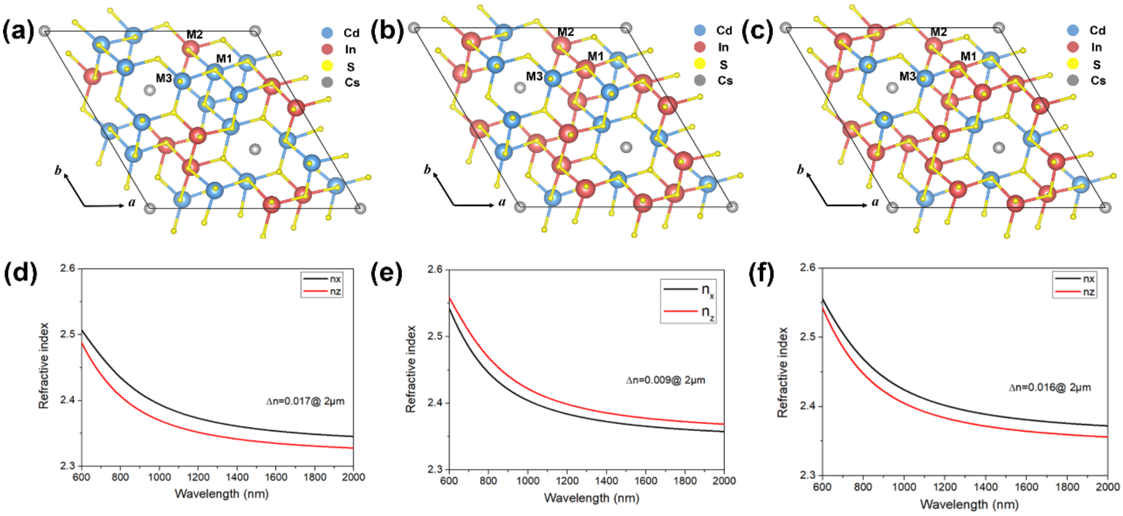

Figure S5. Structure models of $CsCd_4In_5S_{12}$ used for calculation. A structure model with the disordered sites (the site M1 marked in Figure R4a) occupied by Cd (a) or by Cd and In in a ratio of 1:2 (b) or all by In atoms (c). Calculated refractive dispersion curve of $CsCd_4In_5S_{12}$ model a (d), model b (e) and model c (f).

In these models, the M3 site is all occupied with Cd atoms while the M2 site is full filled with In atoms. According to the different situation of the occupation of M1 site, three models were calculated. In Figure S5, the M1 site in three models was all occupied by Cd (M1 = $(Cd3)_{1/3}$) or In (M1 = $(In3)_{1/3}$) atoms or filled with Cd and In in a ratio of 1:2 (M1 = $(CdIn2)_{1/3}$, *P*1 symmetry model).

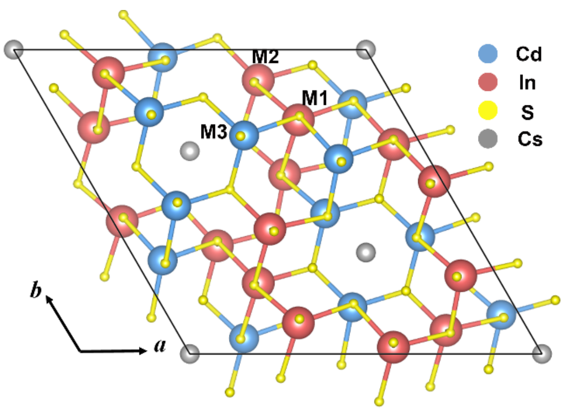

Figure S6. A structure model of $CsCd_4In_5S_{12}$ used for calculation.

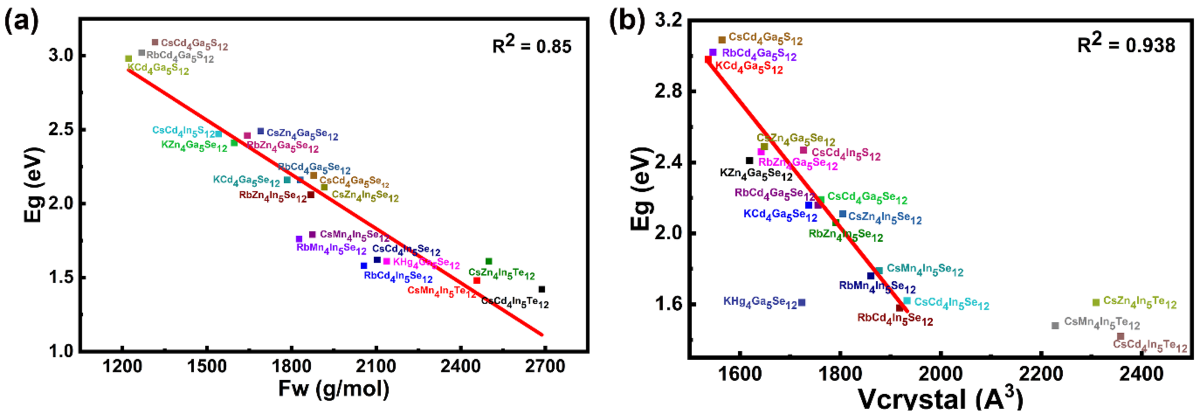

Figure S7. Eg vs the relative molecular mass (a) and Eg vs the volume (b) of compounds in the A-X^{II}_4-X^{III}_5-Q_{12} system

Table S1. EDS results of $CsCd_4In_5S_{12}$.

Element	Weight%	Atomic%
S K	22.78	51.59
Cd L	28.69	18.53
In L	39.13	24.74
Cs L	9.40	5.14
Totals	100.00	100.00

Table S2. The unit cell volume, SHG response at the particle size in the range of 150 – 200 μm, band gaps and LIDT of compounds have been discovered in the A-X^{II}_4-X^{III}_5-Q_{12} system.

Compounds	V_{crstal} (Å^3)	SHG (× AGS)	Eg (eV)	LIDT (× AGS)
[1]$KCd_4Ga_5S_{12}$	1536.7	2.1	2.98	/
[1]$RbCd_4Ga_5S_{12}$	1546.5	1.8	3.02	/
[1]$CsCd_4Ga_5S_{12}$	1564.3	1.6	3.09	/
[2]$KZn_4Ga_5Se_{12}$	1619.48	3.7	2.41	23.4
[2]$RbZn_4Ga_5Se_{12}$	1642.3	3.1	2.46	20.5
[2]$CsZn_4Ga_5Se_{12}$	1649	2.8	2.49	19.2
[3]$KHg_4Ga_5Se_{12}$	1723.7	20	1.61	/
***$CsCd_4In_5S_{12}$**	1726.7	1.08	2.47	9.29
[4]$KCd_4Ga_5Se_{12}$	1737.1	4.5	2.16	/
[4]$RbCd_4Ga_5Se_{12}$	1755.6	2.5	2.16	/
[4]$CsCd_4Ga_5Se_{12}$	1761.3	2	2.19	/
[5]$RbZn_4In_5Se_{12}$	1791.4	3.9	2.06	13
[5]$CsZn_4In_5Se_{12}$	1804.7	3.5	2.11	13
[4]$RbMn_4In_5Se_{12}$	1861.1	5.2	1.76	/
[4]$CsMn_4In_5Se_{12}$	1877.2	4.8	1.79	/
[4]$RbCd_4In_5Se_{12}$	1918.1	7.2	1.58	/
[4]$CsCd_4In_5Se_{12}$	1932.9	6	1.62	/
[6]$CsMn_4In_5Te_{12}$	2228	0.24	1.48	/
[6]$CsZn_4In_5Te_{12}$	2309.2	0.83	1.61	/
[6]$CsCd_4In_5Te_{12}$	2358.4	1.43	1.42	/

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Table S3. Atomic coordinates and equivalent isotropic displacement parameters of $CsCd_4In_5S_{12}$.

Atom	**Wyck.**	***x/a***	***y/b***	***z/c***	U_{eq} [Å^2]	**Occu.**
Cs	3*a*	-1/3	-2/3	0.30157(6)	0.0327(3)	1
Cd1/In1	9*b*	0.40971(8)	-0.02587(7)	0.05075(4)	0.0161(3)	0.367/0.633
Cd2/In2	9*b*	0.43289(9)	0.41079(10)	0.71363(2)	0.0174(4)	0.462/0.538
Cd3/In3	9*b*	0.53833(4)	0.15344(4)	0.38778(3)	0.0171(6)	0.505/0.495
S1	9*b*	0.41281(9)	-0.03548(1)	0.30635(1)	0.0158(8)	1
S2	9*b*	0.54744(1)	0.16472(9)	0.64340(1)	0.0159(8)	1
S3	9*b*	0.29560(1)	0.22602(1)	0.63586(1)	0.0164(6)	1
S4	9*b*	0.38396(1)	0.54050(1)	0.61658(1)	0.0167(8)	1

Table S4. Selected bond lengths (Å) of $CsCd_4In_5S_{12}$.

$CsCd_4In_5S_{12}$	**Length (Å)**
Cd1/In1 – S1	2.481(7)
Cd1/In1 – S1^{II}	2.492(2)
Cd1/In1 – S2	2.483(9)
Cd1/In1 – S3	2.492(3)
Cd2/In2 – S2	2.493(3)
Cd2/In2 – S3	2.494(0)
Cd2/In2 – S3^{II}	2.496(6)
Cd2/In2 – S4	2.476(3)
Cd3/In3 – S1	2.512(1)
Cd3/In3 – S2	2.491(4)
Cd3/In3 – S4	2.493(8)
Cd3/In3 – S4^{II}	2.494(7)
Cs1 – S1 × 3	3.824(4)
Cs1 – S2 × 3	3.822(0)

Cs1 – S3 × 3	3.831(9)
Cs1 – S4 × 3	3.806(5)