Supporting information for

$Ba_6Li_2CdSn_4S_{16}$: Lithium Substitution Enhances Band Gap and SHG Intensity Simultaneously

Rui-Huan Duan,[a,b] Peng-Fei Liu,[a,b] Hua Lin,[b] Y. J. Zheng,[a,b] Ju-Song Yu,[a,b] Xin-Tao Wu,[a] Shang-Xiong Huang-Fu[c] and Ling Chen*[a]

a Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China

b University of Chinese Academy of Sciences, Beijing 100039, People's Republic of China

c Physics Institute of the University of Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland

*E-mail: chenl@fjirsm.ac.cn. Tel: +(011)86-591-63173211.

Table S1. Atomic coordinates, equivalent isotropic displacement parameters and occupancies of $Ba_6Li_2CdSn_4S_{16}$ (**1**) and $Ba_6Ag_2CdSn_4S_{16}$ (**2**).

Atom	Oxidation	Wyckof	x	y	z	U(eq)	sof
				1			
Ba1	+2	24*d*	0.0000	0.2500	0.23438(2)	0.0180(2)	1
Sn1	+4	16*c*	0.27194(2)	0.27194(2)	0.27194(2)	0.0117 (2)	1
Cd1	+2	12*b*	-0.1250	0.0000	0.2500	0.0152(5)	0.33
Li1	+1	12*b*	-0.1250	0.0000	0.2500	0.0152(5)	0.67
S1	–2	16*c*	0.11484(8)	0.11484(8)	0.11484(8)	0.0190(4)	1
S2	–2	48*e*	-0.06702(6)	0.08283(7)	0.38842(6)	0.0146(2)	1
				2			
Ba1	+2	24*d*	0.0000	0.2500	0.01795(2)	0.01873(7)	1
Sn1	+4	16*c*	0.02136(2)	0.52136(2)	-0.02136(2)	0.01132(8)	1
Cd1	+2	12*a*	-0.1250	0.5000	-0.2500	0.054(2)	0.33
Ag1	+1	12*a*	-0.1250	0.5000	-0.2500	0.0197(6)	0.67
S1	–2	16*c*	-0.13655(4)	0.36345(4)	0.13655(4)	0.0178(2)	1
S2	–2	48*e*	-0.06582(4)	0.41464(4)	-0.10877(4)	0.0140(2)	1

Table S2. Selected bond lengths (Å) and angles (deg) for compounds **1** and **2**.

1		**2**	
Ba1-S1×2	3.1372(7)	Ba1-S1×2	3.1467(5)
Ba1-S2×2	3.2342(9)	Ba1-S2×2	3.2120(5)
Ba1-S2×2	3.2944(9)	Ba1-S2×2	3.3054(6)
Ba1-S2×2	3.476(2)	Ba1-S2×2	3.5118(7)
Sn1-S1	2.360(2)	Sn1-S1	2.351(2)
Sn1-S2×3	2.407(2)	Sn1-S2×3	2.4051(6)
Li/Cd1-S2×4	2.5143(9)	Ag/Cd1-S2×4	2.5838(6)
S1-Sn1-S2×3	111.48(3)	S1-Sn1-S2×3	112.13(2)
S2-Sn1-S2×3	107.39(3)	S2-Sn1-S2×3	106.69(2)
S2-Li/Cd-S2×4	96.57(2)	S2-Ag/Cd-S2×4	96.44(9)
S2-Li/Cd-S2×2	140.46(4)	S2-Ag/Cd-S2×2	140.54(3)

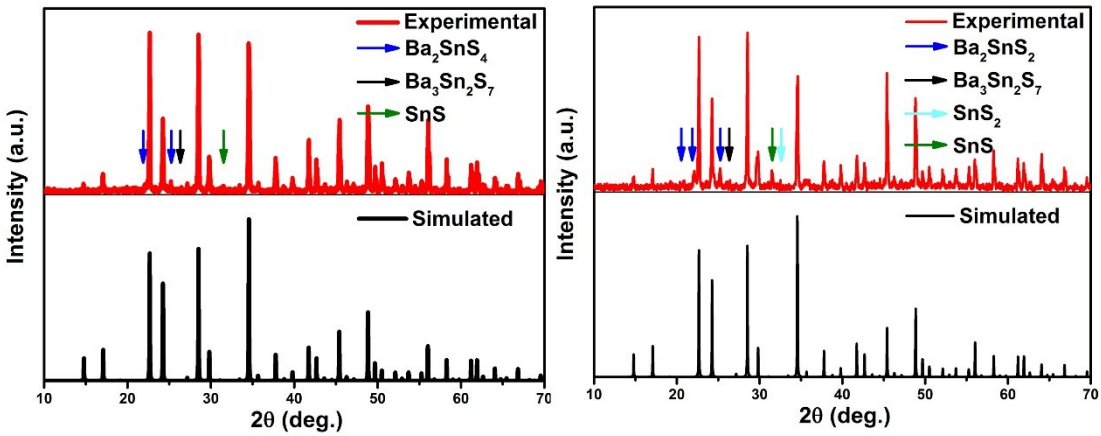


Figure S1. Experimental XRD patterns of compound **1** with more (a) and less (b) Li_2S.

The black arrow shows impurity phases.

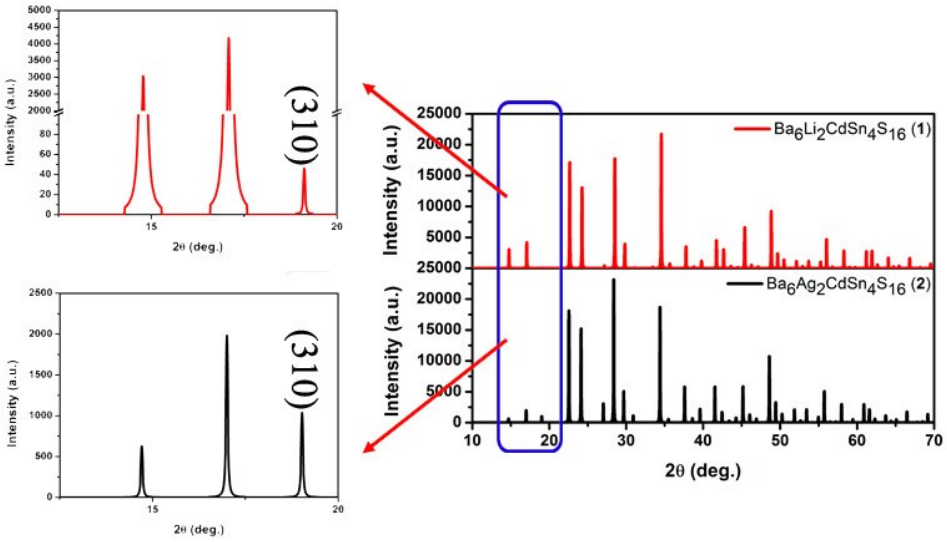
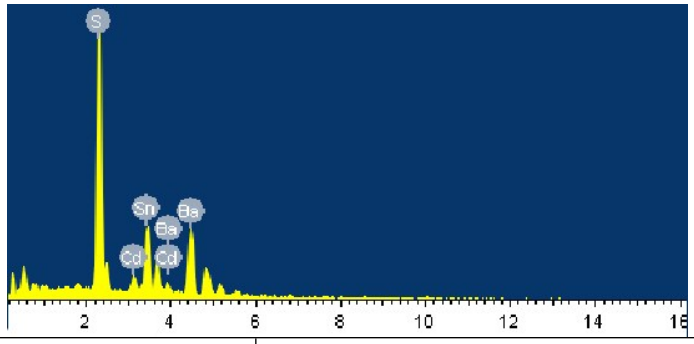


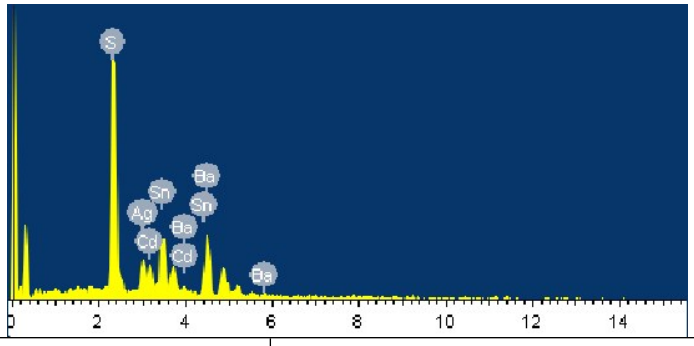
Figure S2. The simulated powder X-ray diffraction (XRD) patterns for

$Ba_6Li_2CdSn_4S_{16}$ (**1**) and $Ba_6Ag_2CdSn_4S_{16}$ (**2**).



Point-1				Point-2			
Element	Weight%	Atomic%	Formular	Element	Weight%	Atomic%	Formular
S	26.02	58.31	14.54	S	24.70	56.77	14.34
Cd	6.27	4.01	1.00	Cd	6.04	3.96	1.00
Sn	27.56	16.68	4.15	Sn	25.05	15.55	3.99
Ba	40.15	21.00	5.25	Ba	44.20	23.72	5.99
Totla	100.0			Totla	100		
Point-3				Point-4			
Element	Weight%	Atomic%	Formular	Element	Weight%	Atomic%	Formular
S	26.01	59.03	14.72	S	26.90	59.51	16.39
Cd	6.30	4.04	1.00	Cd	5.75	3.63	1.00
Sn	26.53	15.83	3.91	Sn	25.21	14.90	4.10
Ba	41.86	21.72	5.38	Ba	41.82	21.61	5.95
Totla	100.0			Totla	100		
Point-5							
Element	Weight%	Atomic%	Formular				
S	27.85	60.53	15.65				
Cd	6.24	3.87	1.00	Average Formular			
Sn	27.11	15.92	4.11	$Ba_{5.53}Cd_{1.00}Sn_{4.05}S_{15.13}$			
Ba	38.79	19.68	5.09				
Totla	100.0						

Figure S3. EDX spectrum of $Ba_6Li_2CdSn_4S_{16}$



Point-1				Point-2			
Element	Weight%	Atomic%	Formular	Element	Weight%	Atomic%	Formular
S	22.81	53.43	15.58	S	22.53	53.03	15.50
Ag	10.76	7.49	2.18	Ag	12.05	8.43	2.30
Cd	6.16	4.12	1.20	Cd	5.46	3.67	1.04
Sn	23.33	14.76	4.20	Sn	22.39	14.23	4.07
Ba	36.94	20.20	5.90	Ba	37.56	20.64	5.89
Totla	100.0			Totla	100		
Point-3				Point-4			
Element	Weight%	Atomic%	Formular	Element	Weight%	Atomic%	Formular
S	22.42	52.95	15.49	S	22.98	53.69	15.56
Ag	10.53	7.39	2.11	Ag	11.35	7.88	2.21
Cd	5.42	3.65	1.02	Cd	6.78	4.52	1.21
Sn	23.43	14.95	4.20	Sn	20.87	13.17	3.90
Ba	38.19	21.05	6.01	Ba	38.02	20.74	6.01
Totla	100.0			Totla	100		
Point-5							
Element	Weight%	Atomic%	Formular	Average Formular $Ba_{5.97}Ag_{2.15}Cd_{1.07}Sn4.11S_{15.60}$			
S	23.68	54.78	15.88				
Ag	10.01	6.88	1.99				
Cd	4.67	3.08	0.91				
Sn	23.18	14.48	4.19				
Ba	38.46	20.77	6.02				
Totla	100.0						

Figure S4. EDX spectrum of $Ba_6Ag_2CdSn_4S_{16}$

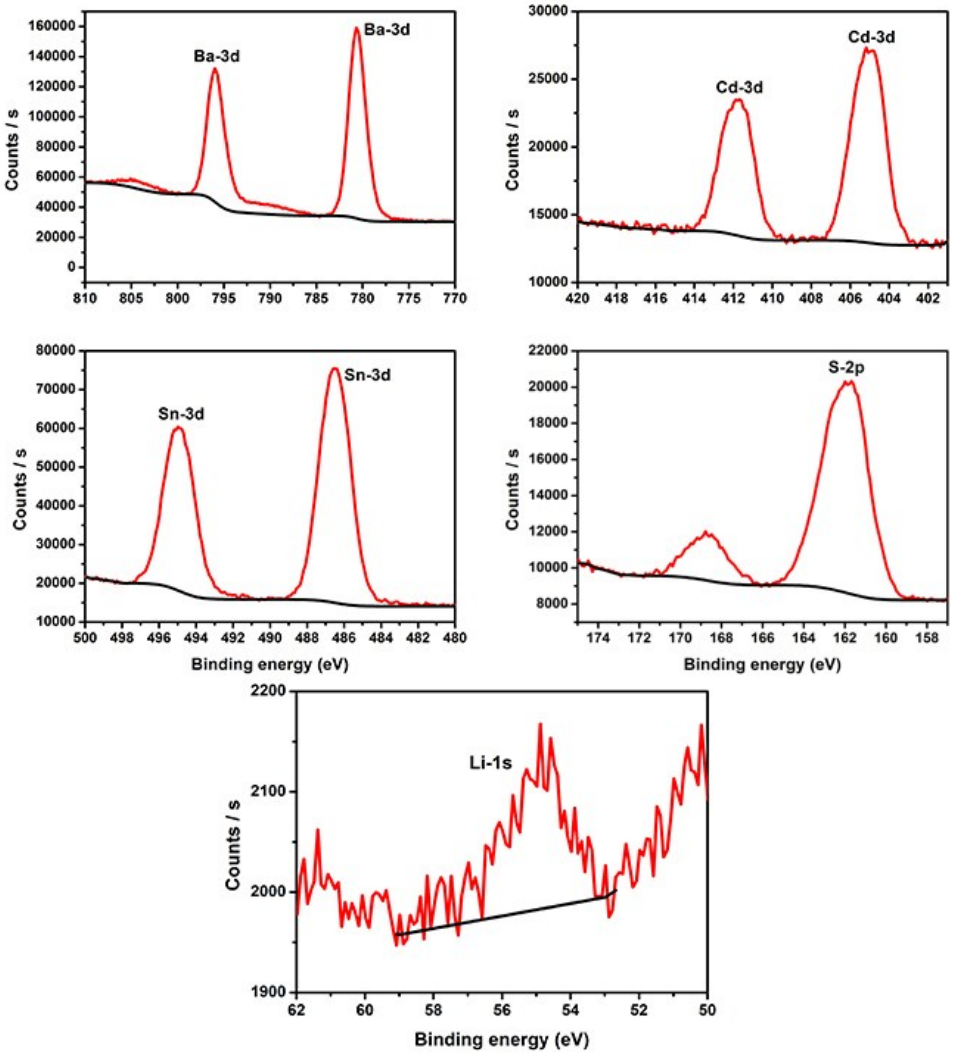


Figure S5. XPS of $Ba_6Li_2CdSn_4S_{16}$.

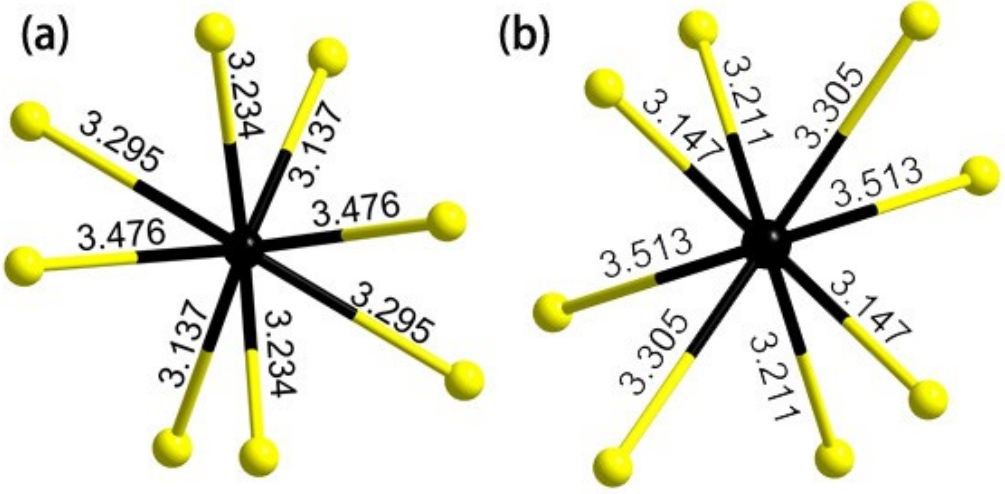


Figure S6. The environment of Ba atom in compounds **1** (a) and **2** (b).

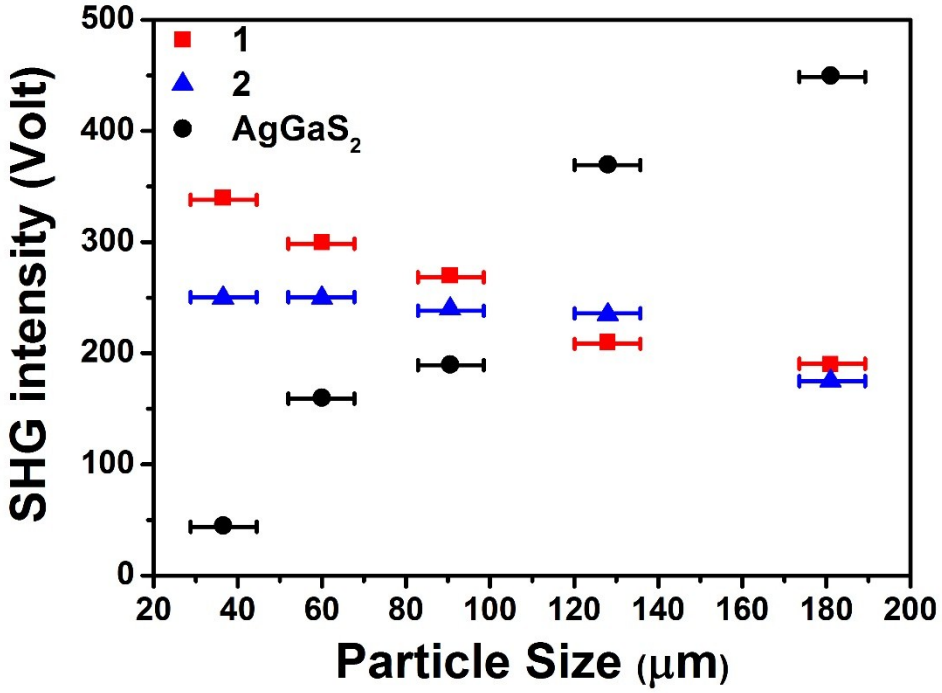


Figure S7. The SHG vs particle size patterns of compounds **1**, **2** and $AgGaS_2$ at 2.05μm.

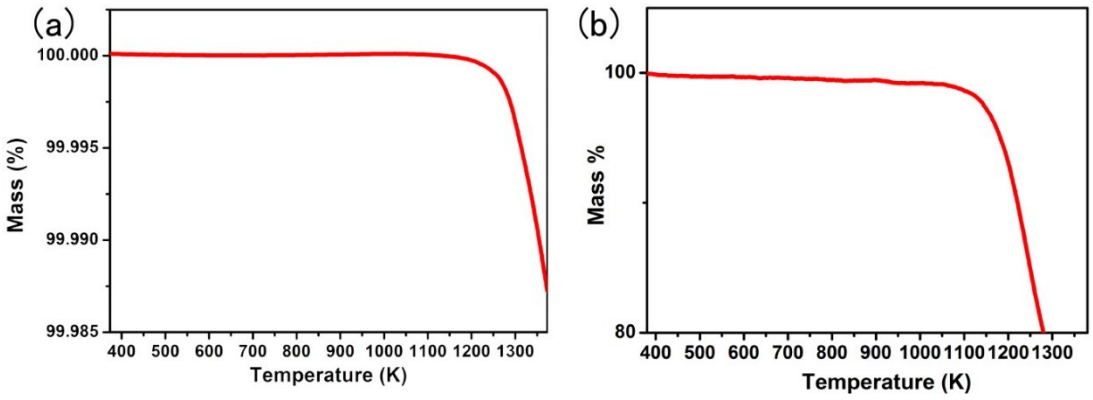


Figure S8. The TGA patterns of compounds **1** (a) and **2** (b) under N_2 flow.

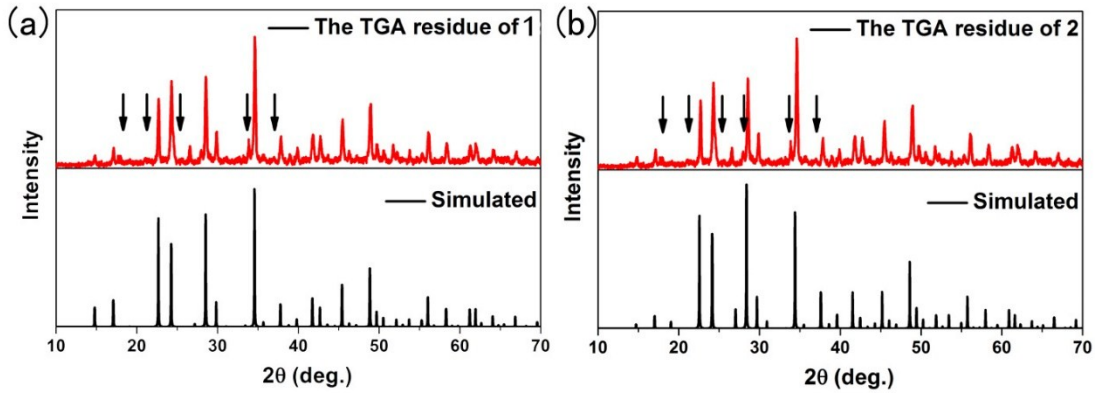


Figure S9. The powder-XRD patterns of TGA residues of compounds **1** and **2** under N_2 atmosphere. The black arrow shows impurity phases.

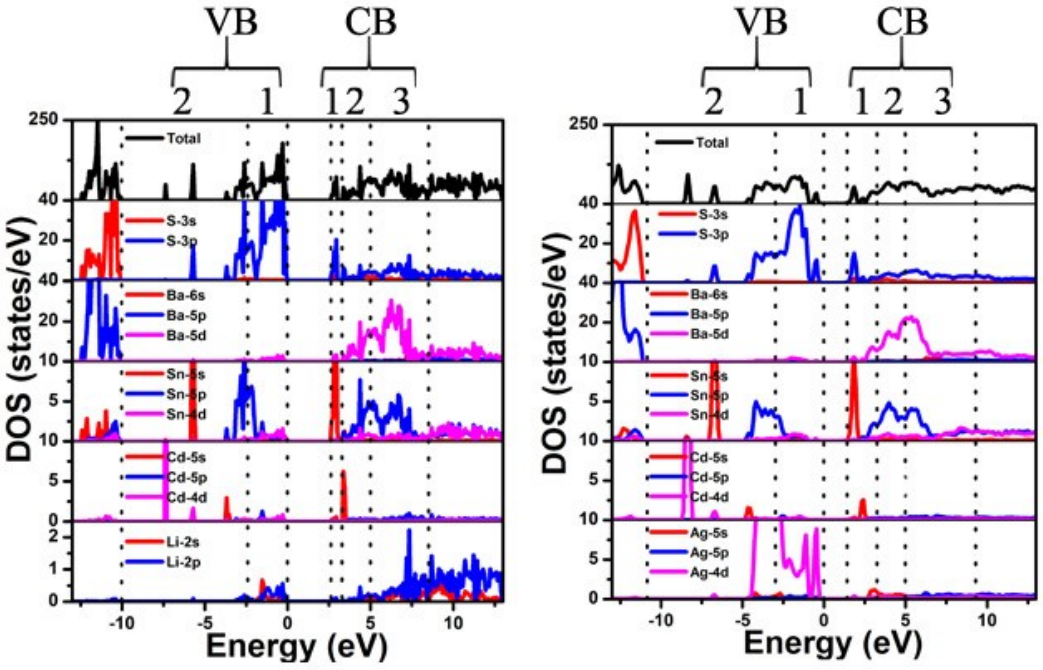


Figure S10. Total and partial DOS of compounds **1** (a) and **2** (b).

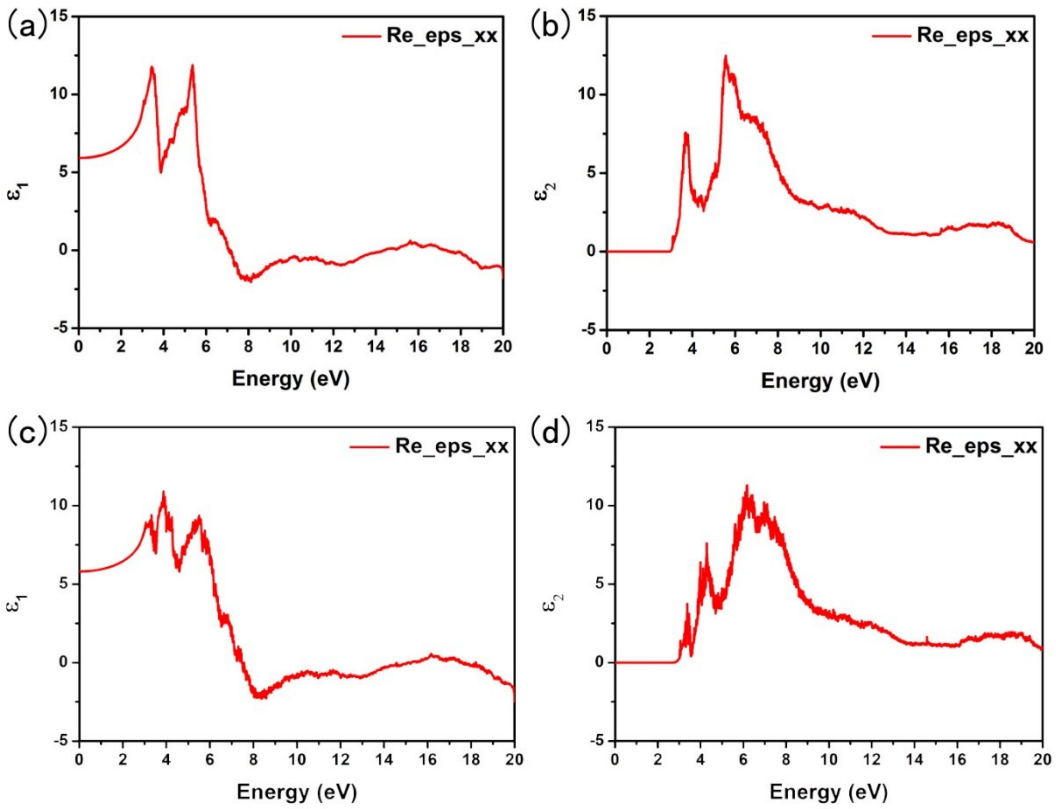


Figure S11. Energy dependences of the real part ε_1 and imaginary part ε_2 of compounds **1** ((a) and (b)) and **2** ((c) and (d)).

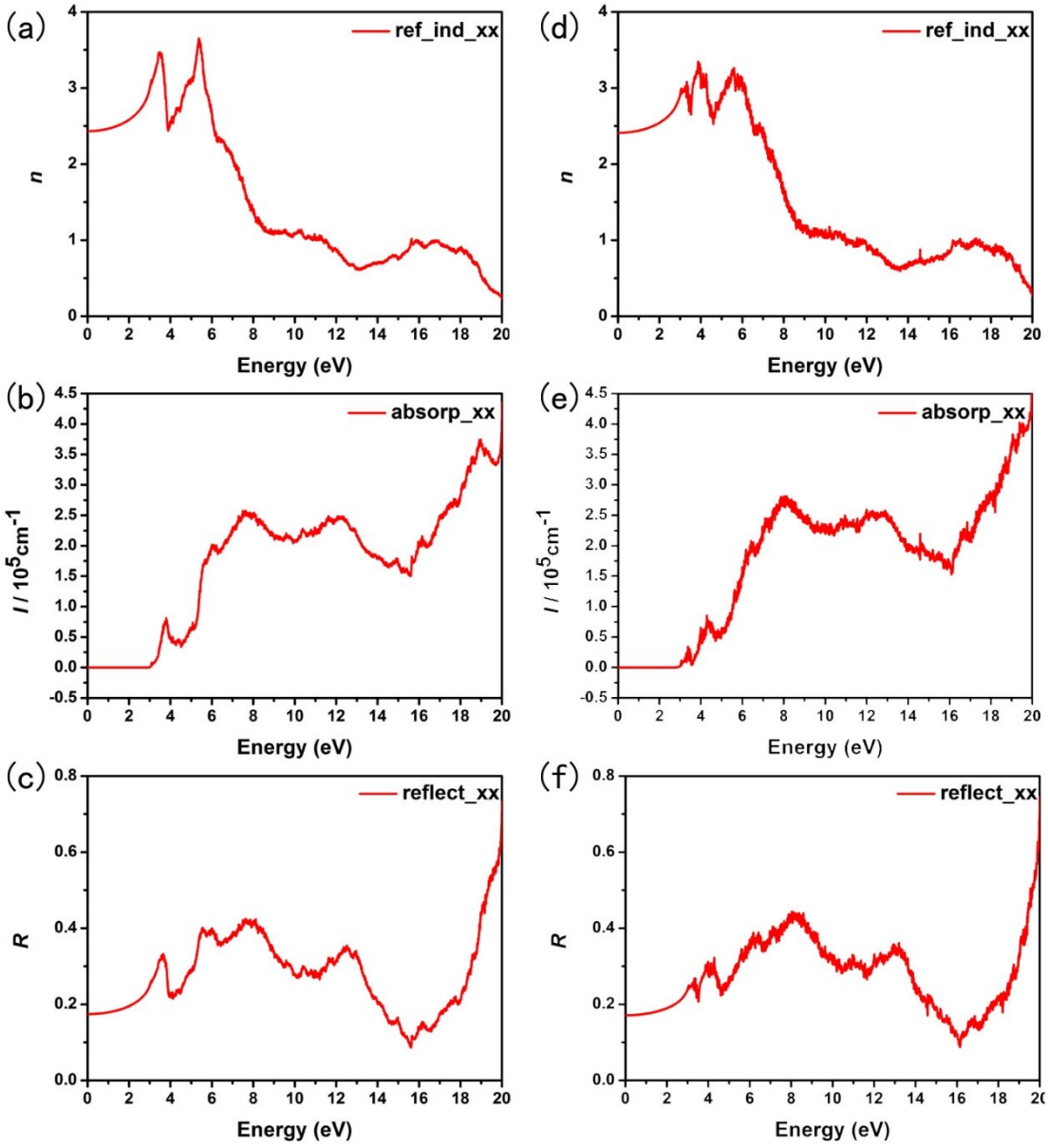


Figure S12. The calculated optical properties, Variations of the refractive index *n*, The reflectivity *R* and The absorption coefficient *I* for compounds **1** ((a), (b) and (c))and **2** ((d), (e) and (f)).

Electronic Structure Calculations. Compounds **1** and **2** belong to the point group $\bar{4}3m$ and thus have one nonvanishing second-order susceptibility tensors (χ_{14}) under the restriction of Kleinman's symmetry. According to the single crystal structure refinement results with the disorder of Li and Cd in compound **1**, a model with *P*1 symmetry was built, which has ten independent second-order susceptibility tensors with the restriction of Kleinman's symmetry (χ_{11}, χ_{12}, χ_{13}, χ_{14}, χ_{15}, χ_{16}, χ_{22}, χ_{23}, χ_{24} and χ_{33}). Among them, with the highest values of second-order coefficient d_{23} (correspond to χ_{23}), they are studied. Meanwhile, the same operations are also carried on **2**.

Figure S11 shows the macroscopic linear optical properties of compound **1** and **2**. The primary peaks of imaginary part $\varepsilon_2(\omega)$ of the dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ for **1** and **2** are near 5.57 and 3.90 eV, respectively, which can be mostly considered as interband transitions from the S-3p to Ba-5d and Sn-5p states. Nevertheless, the interband transition between the occupied and unoccupied states is only important in metallic compounds, which can be ignored.[1] The calculated value of $\varepsilon_1^{ave}(0)$ which is the average values of polarized zero-frequency dielectric constants are 5.92 and 5.81, respectively, with the equation $\varepsilon_1(0) = 1/3\ [\varepsilon_{1xx}(0) + \varepsilon_{1yy}(0) + \varepsilon_{1zz}(0)]$. In addition, the refractive index $n(\omega)$, absorption coefficient $I(\omega)$ and reflectivity $R(\omega)$ were shown in Figure S12. The function $n(\omega)$ of **1** and **2** show its peak near 5.3 and 5.6 eV, and all decrease rapidly in the range from 6.0 to 13.0 eV, matching mainly with their higher values for $R(\omega)$ in this region. Due to the free carrier adsorptions in semiconductors,[2] $I(\omega)$ is about 10^5 cm^{-1} and the calculated absorption edge for **1** and **2** are 2.94 and 2.70 eV, respectively.

Reference

1. (a) P. Ravindran, A. Delin, R. Ahuja, B. Johansson, S. Auluck, J. M. Wills, O. Eriksson, *Phys. Rev. B*, 1997, **56**, 6851. (b) H. Haiying, R. Orlando, M. A. Blanco, R. Pandey, E. Amzallag, I. Baraille, M. Rerat, *Phys. Rev. B*, 2006, **74**, 195123.
2. D. Vanmaekelbergh, L. van Pieterson, *Phys. Rev. Lett.*, 1998, **80**, 821.