Two rare-earth-based quaternary chalcogenides $EuCdGeQ_4$ (Q = S, Se) with strong second-harmonic generation

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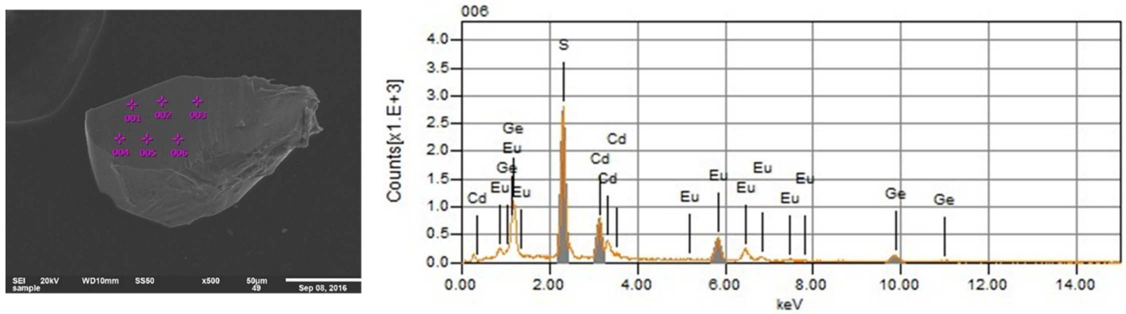
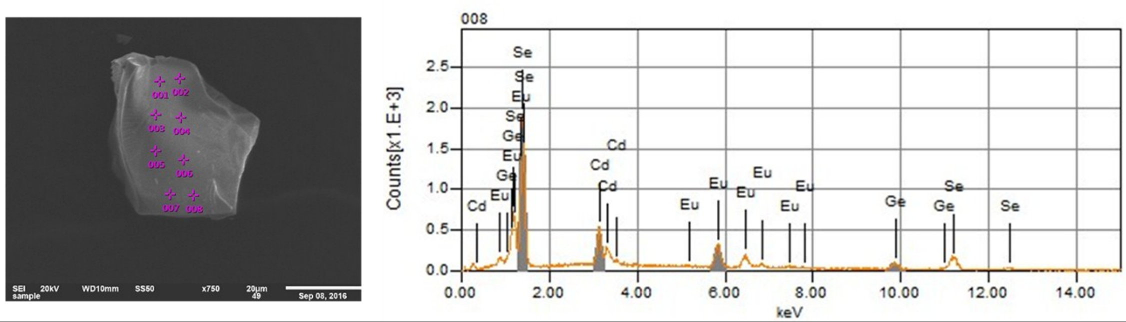


Number / elements	1 (mol%)	2(mol%)	3 (mol%)	4 (mol%)	5 (mol%)	6 (mol%)
Eu	14.50	14.44	14.20	13.78	14.72	13.83
Cd	14.27	14.15	14.50	14.30	14.72	14.59
Ge	15.06	15.06	15.25	17.34	13.72	14.39
S	56.17	56.36	56.05	54.58	56.85	57.19

Figure S1. The EDX analysis of $EuCdGeS_4$.



Number / elements	1 (mol%)	2(mol%)	3 (mol%)	4 (mol%)	5 (mol%)	6 (mol%)
Eu	13.83	12.57	13.26	12.32	14.33	15.27
Cd	14.73	14.07	14.35	14.62	14.79	14.32
Ge	11.02	14.33	14.27	14.32	13.98	14.06
Se	60.41	60.03	58.12	58.74	56.90	56.35

Figure S2. The EDX analysis of $EuCdGeSe_4$.

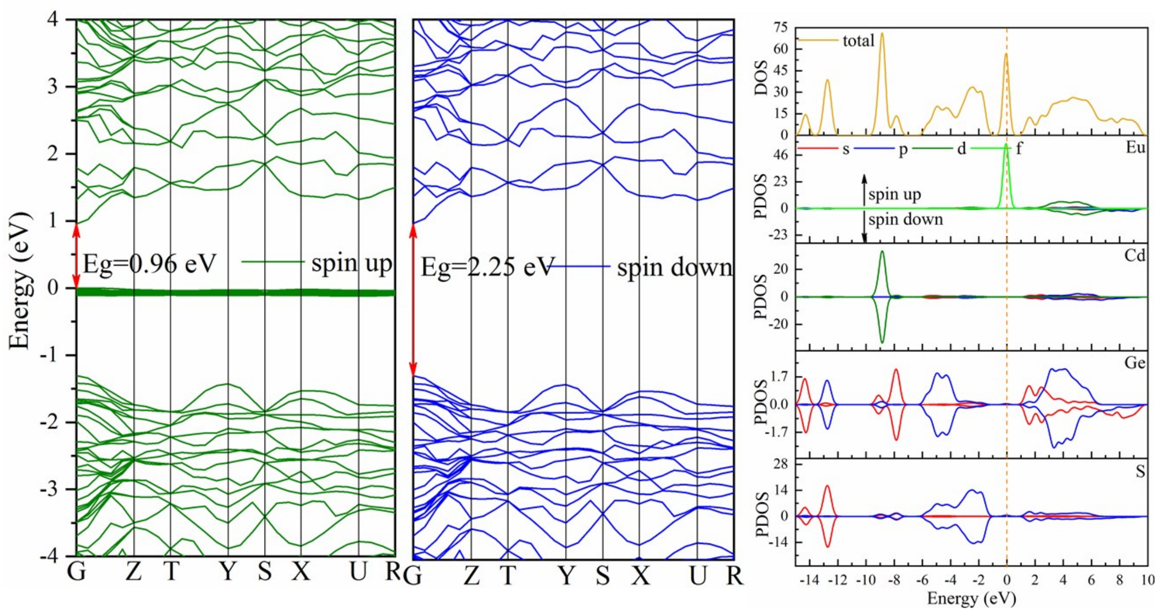


Figure S3. The calculated band structure and the density of states (DOS) of $EuCdGeS_4$
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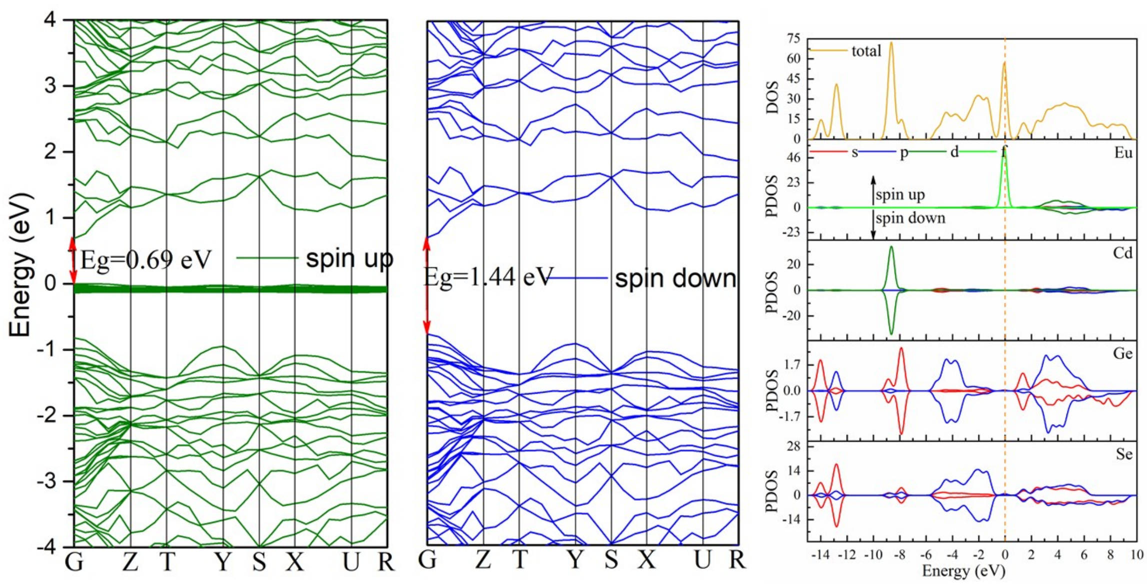

Figure S4. The calculated band structure and the density of states (DOS) of $EuCdGeSe_4$.

Synthesis of EuQ (Q = S, Se)

The binary materials EuQ (Q = S, Se) were synthesized by stoichiometric reactions of the elements within the sealed silica tubes. In the preparation of EuQ (Q = S, Se), the fused-silica tubes were carbon-coated to avoid deleterious reactions with elemental Eu. The tubes were heated to 1273 K for EuS and 1223 K EuSe in 10 h, maintained the temperature for 48 h, and cooling down to room temperature by shuting off the furnace. In order to enhance the crystallinity and purity, regrinding and a repeated heat treatment were necessary for the samples. Eventually, dark powder of EuS and dark red powder of EuSe were obtained. They showed high crystallinity and purity according to the PXRD patterns, which agreed well with patterns simulated from the reported single-crystal structure. [1]

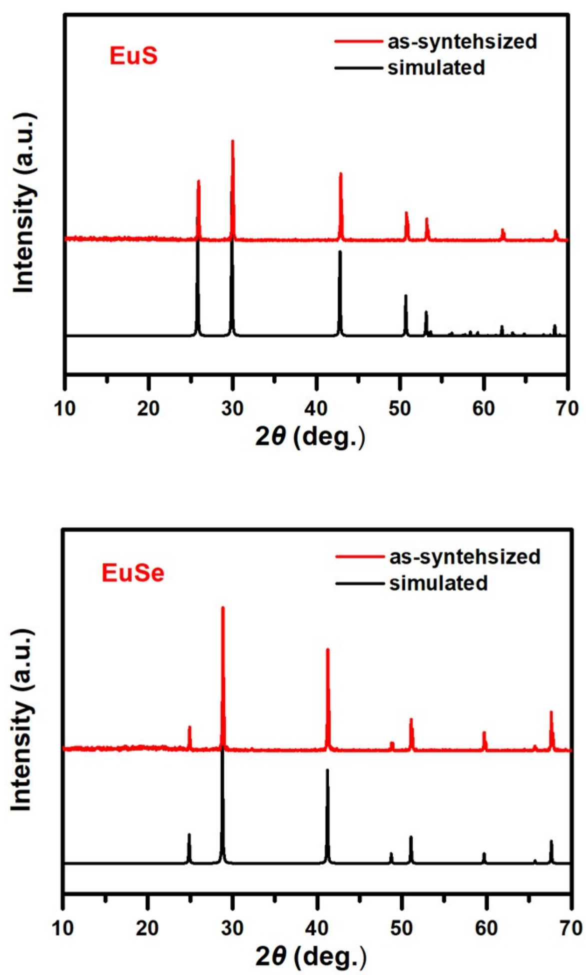

Figure S5. Powder XRD patterns of EuQ (Q = S, Se).

Table S1. Bond valence sums for $EuCdGeS_4$ and $EuCdGeSe_4$.

$EuCdGeS_4$	Eu	Cd	Ge	S1	S2	S3
BVS	2.01	1.96	3.97	1.87	2.071	1.933
$EuCdGeSe_4$	Eu	Cd	Ge	Se1	Se2	Se3
BVS	1.78	1.91	3.90	1.86	2.26	2.11

Table S4. Space groups and optical performances of $A^{II}M^{II}M^{IV}Q_4$ (A^{II} = alkaline-earth metal; M^{II} = Zn, Cd, Hg, Mn; MIV = Si, Ge, Sn; Q = S, Se).

Materials	Space Group	Eg (eV)	SHG (×$AgGaS_2$)	Phase-matching	congruent-melting	Ref.
$BaZnSiSe_4$	*Ama*2	2.71	1/3@41-74um	-	-	[2]
$BaZnGeSe_4$	*Ama*2	2.46	1	yes	-	[2]
$BaCdSnS_4$	*Fdd*2	2.30	0.7	no	-	[3]
$BaCdSnSe_4$	*Fdd*2	1.79	1.6	no	-	[4]
$SrCdGeS_4$	*Ama*2	2.6	1.7	yes	987/946	[5]
$SrCdGeSe_4$	*Ama*2	1.9	5.3	yes	885/833	[5]
$SrZnSnS_4$	*Fdd*2	3.37	1×$LiGaS_2$	yes	No	[6]
$SrCdSnS_4$	*Fdd*2	2.05	1.3	yes	889/790	[7]
$SrCdSnSe_4$	*Fdd*2	1.54	1.5	yes	786/688	[7]
$BaHgGeSe_4$	*Ama*2	2.49	4.7	yes	732/589	[8]
$SrHgGeSe_4$	*Ama*2	2.42	4.8	yes	745/684	[8]
β-$BaHgSnS_4$	*Ama*2	2.77	2.8	yes	no	[9]
$SrHgSnS_4$	*Ama*2	2.72	1.9	yes	no	[9]
$BaHgSnSe_4$	*Fdd*2	1.98	5.1	yes	712/675	[9]
$SrHgSnSe_4$	*Fdd*2	2.07	4.9	yes	no	[9]
$BaMnSnS_4$	*Fdd*2	1.9	1.2	yes	829/636	[10]
$BaCdGeS_4$	*Fdd*2	2.58	0.3	yes	921/677	[10]
$EuCdGeS_4$	*Ama*2	2.5	2.6	yes	997/864	This work
$EuCdGeSe_4$	*Ama*2	2.25	3.8	yes	882/723	This work

"-" means no data available.

Table S3. Bond lengths for $EuCdGeS_4$ and $EuCdGeSe_4$.

$EuCdGeS_4$		$EuCdGeS_4$	
Bonds	Length / Å	Bonds	Length / Å
Eu–S1 (×2)	3.1530	Eu–Se1 (×2)	3.2114
Eu–S1 (×2)	3.1314	Eu–Se2 (×2)	3.2643
Eu–S2 (×2)	3.0106	Eu–Se2 (×2)	3.2605
Eu–S3 (×2)	3.1051	Eu–Se3 (×2)	3.1405
Ge–S1 (×2)	2.2250	Ge–Se1	2.328
Ge–S2	2.240	Ge–S2 (×2)	2.3657
Ge–S3	2.191	Ge–Se3	2.379
Cd–S1 (×2)	2.5951	Cd–Se1	2.789
Cd–S2	2.449	Cd–Se2 (×2)	2.6906
Cd–S3	2.670	Cd–S3	2.5627

Table S4. Selected bond angles for $EuCdGeS_4$ and $EuCdGeSe_4$.

$EuCdGeS_4$			
Bonds	Angle /	Bonds	Angle /
S1—Eu—S1^{i}	70.424	S3^{iv}—Eu—S1^{iii}	79.64
S1—Eu—S1^{iii}	146.82	S3^{v}—Eu—S1	87.84
S1^{ii}—Eu—S1	103.38	S3^{iv}—Eu—S1	33.43
S2—Eu—S1^{i}	131.74	S3^{iv}—Eu—S3^{v}	116.78
S2^{ii}—Eu—S3^{v}	148.86	S1^{iii}—Ge—S1^{vii}	105.02
S2—Eu—S2^{ii}	131.44	S1^{vii}—Ge—S2	105.84
S2—Eu—S1^{iii}	70.56	S3—Ge—S1^{iii}	117.12
S2—Eu—S1^{ii}	74.07	S3—Ge—S2	104.85
S2—Eu—S3^{v}	64.86	S1^{x}—Cd—S1^{ix}	85.74
S1^{i}—Eu—S1^{iii}	132.24	S1^{ix}—Cd—S3^{xi}	93.85
S2^{ii}—Eu—S1^{ii}	76.38	S2—Cd—S1^{x}	135.12
S3^{iv}—Eu—S1^{i}	75.85	S2—Cd—S3^{xi}	99.54
Symmetry codes: (i) -*x*, -*y*-1/2, *z*-1/2; (ii) -*x*, -*y*, *z*; (iii) *x*, *y*+1/2, *z*-1/2; (iv) -*x*, -*y*+1/2, *z*-1/2; (v) *x*, *y*-1/2, *z*-1/2; (vi) *x*, *y*, *z*-1; (vii) -*x*+1/2, *y*+1/2, 100 *z*-1/2; (viii) *x*, *y*, *z*+1; (ix) *x*, *y*+1/2, *z*+1/2; (x) -*x*+1/2, *y*+1/2, *z*+1/2; (xi) *x*, *y*-1/2, *z*+1/2; (xii) *x*+1/2, -*y*, *z*; (xiii) *x*+1/2, -*y*+1/2, *z*+1/2.			
$EuCdGeSe_4$			
Bonds	Angle /	Bonds	Angle /
Se1i—Eu—Se1	119.31	Se3—Eu—Se2	74.24
Se1—Eu—Se2	86.84	Se3i—Eu—Se2iii	72.48
Se1—Eu—Se2iii	76.73	Se3i—Eu—Se2i	74.25
Se1i—Eu—Se2i	86.84	Se3—Eu—Se3i	130.13
Se1i—Eu—Se2iii	79.33	Se1—Ge—Se2v	117.03
Se1—Eu—Se2i	132.37	Se1—Ge—Se2iv	117.03
Se2iii—Eu—Se2ii	131.53	Se1—Ge—Se3ii	104.41
Se2—Eu—Se2iii	148.17	Se2iv—Ge—Se2v	105.46
Se2—Eu—Se2ii	69.711	Se2v—Ge—Se3ii	105.94
Se2i—Eu—Se2	104.46	Se2iii—Cd—Se1	94.35
Se3—Eu—Se1	150.06	Se2xii—Cd—Se2iii	88.80
Se3i—Eu—Se1	63.85	Se3xiii—Cd—Se1	98.69
Se3—Eu—Se2iii	130.32	Se3xiii—Cd—Se2iii	133.69
Se3i—Eu—Se2	75.83		
Symmetry codes: (i) -*x*+1, -*y*, *z*; (ii) -*x*+1, -*y*+1/2, *z*-1/2; (iii) *x*, *y*-1/2, *z*-1/2; (iv) *x*, *y*, *z*-1; (v) -*x*+3/2, *y*, *z*-1; (vi) *x*+1/2, -*y*, *z*; (vii) *x*, *y*+1/2, *z*+1/2; (viii) *x*, *y*, *z*+1; (ix) *x*-1/2, -*y*, *z*; (x) -*x*+1, -*y*+1/2, *z*+1/2; (xi) -*x*+1, -*y*, *z*+1; (xii) -*x*+3/2, *y*-1/2, *z*-1/2; (xiii) -*x*+1, -*y*, *z*-1.			

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