Electronic Supplementary Information

Two quaternary non-centrosymmetric chalcogenides $BaAg_2GeS_4$ and $BaAg_2SnS_4$: experimental and theoretical studies on the NLO properties

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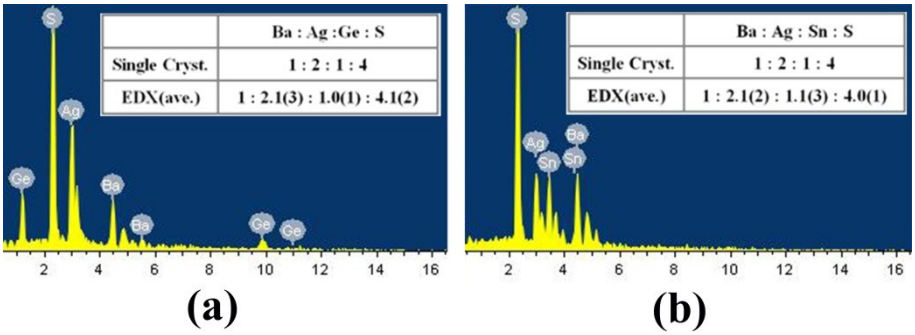

Figure S1 EDX result of (a) $BaAg_2GeS_4$ (**1**) and (b) $BaAg_2SnS_4$ (**2**).

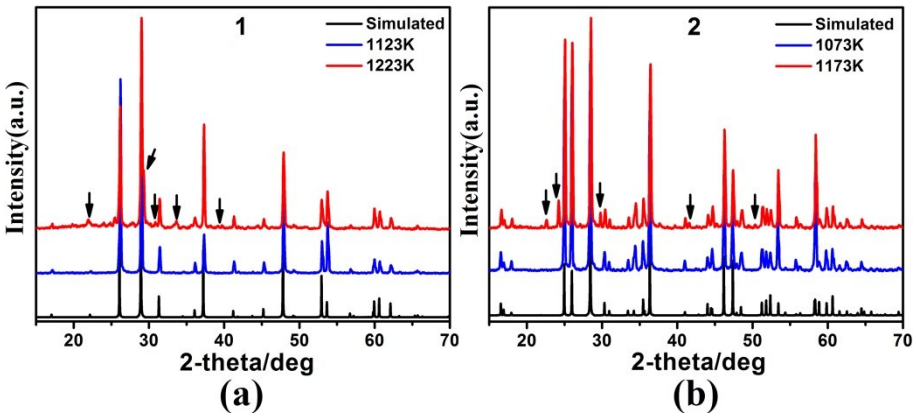

Figure S2 The PXRD patterns of sample of (a) $BaAg_2GeS_4$ (**1**) and (b) $BaAg_2SnS_4$ (**2**) heated at various temperatures (blue and red) and the simulated one (black). For **1**, the sample heated at 1123K was still single phased but decomposed at 1223K. For **2**, the sample heated at 1073K was still single phased but decomposed at 1173K. Arrows indicate the decomposed products.

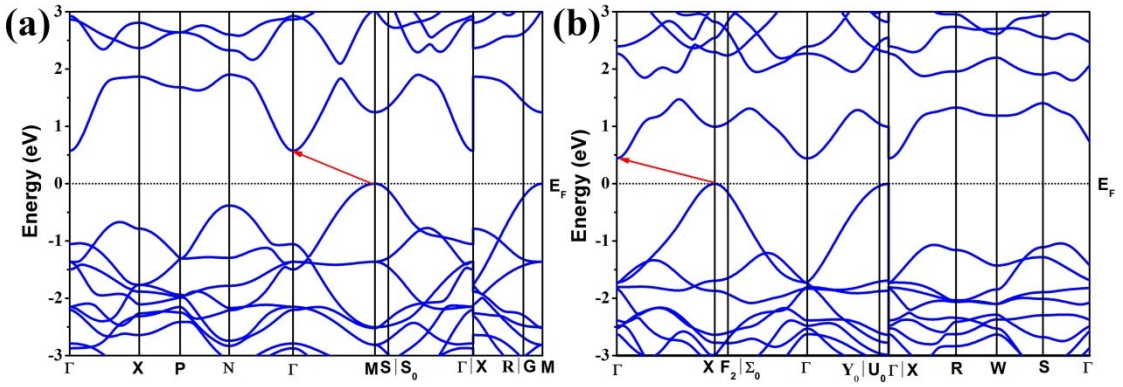

Figure S3 Calculated band structure of (a) $BaAg_2GeS_4$ (**1**) and (b) $BaAg_2SnS_4$ (**2**), the Fermi level is set at 0.0 eV.

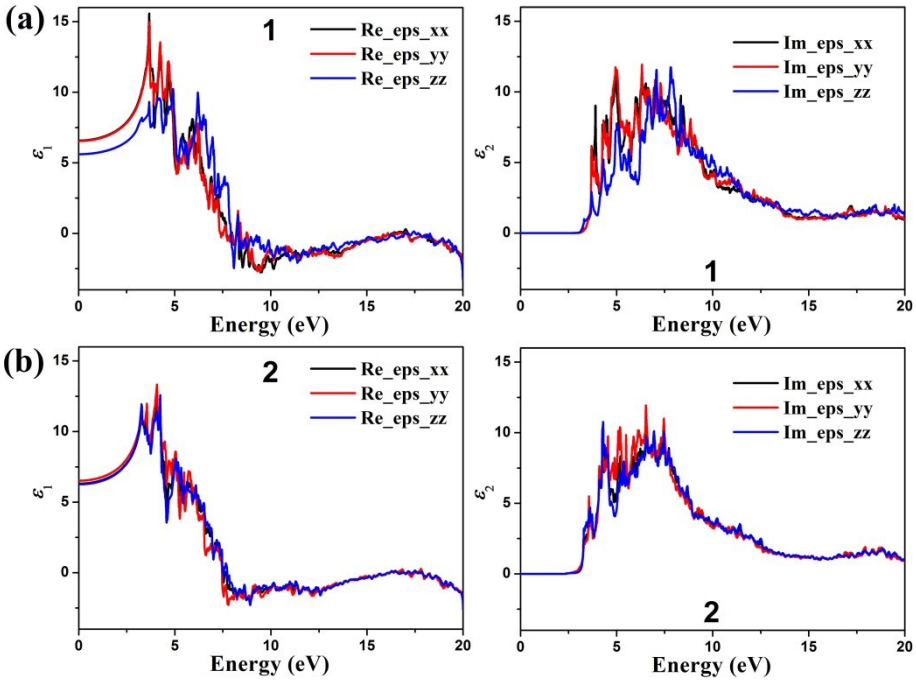

Figure S4. Energy dependences of the real part (ε_1) and imaginary part (ε_2) of (a) $BaAg_2GeS_4$ (**1**) and (b) $BaAg_2SnS_4$ (**2**).

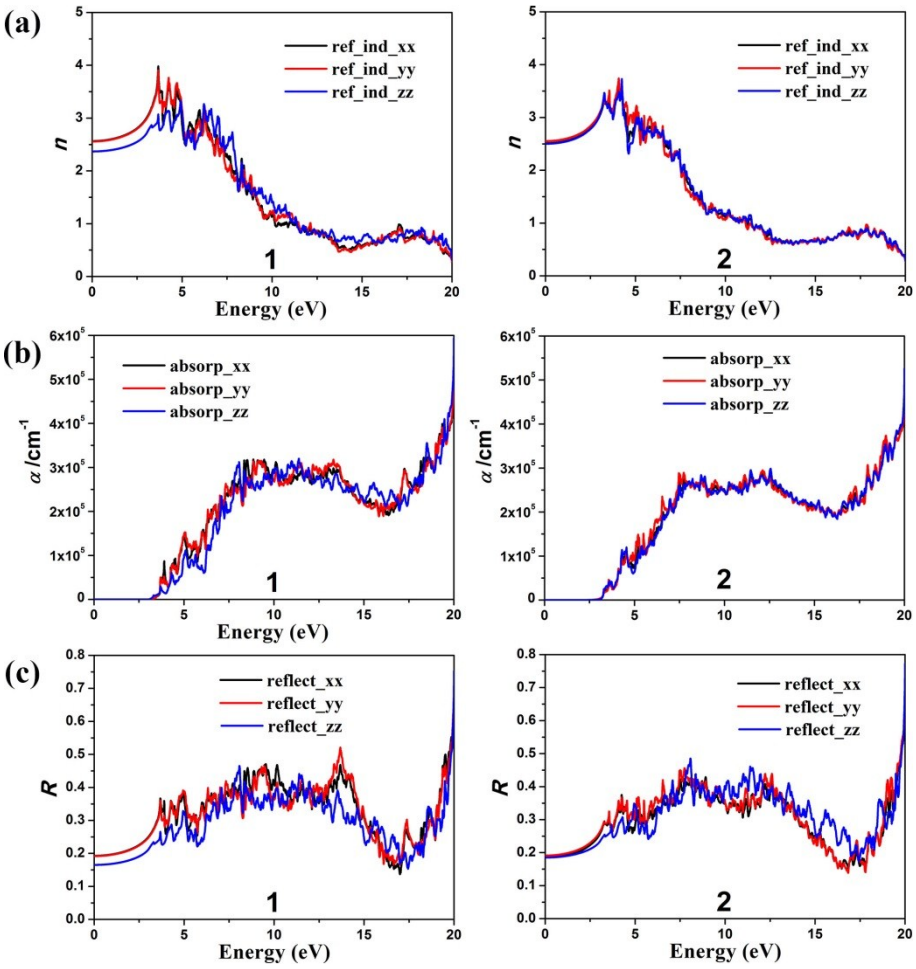

Figure S5. The calculated (a) refractive index (n), (b) absorption coefficient (α) and (c) reflectivity (R) of $BaAg_2GeS_4$ (**1**) and $BaAg_2SnS_4$ (**2**).

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Table S1. Atomic coordinates and equivalent isotropic displacement parameters of $BaAg_2GeS_4$ and $BaAg_2SnS_4$.

Atom	*Wyckoff*	*x*	*y*	*z*	$U_{(eq)}$*
		$BaAg_2GeS_4$			
Ba	2*b*	0	0	0.5	0.0152(7)
Ag	4*d*	0	0.5	0.75	0.0406(8)
Ge	2*a*	0	0	0	0.0112(7)
S	8*i*	0.1889(4)	0.1889(4)	0.1560(4)	0.0157(2)
		$BaAg_2SnS_4$			
Ba	2*a*	0	0	0	0.0165(6)
Ag	4*j*	0	0.5	0.2052(3)	0.0342(7)
Ge	2*c*	0	0	0.5	0.0124(6)
S	8*k*	0.2980(7)	0.3064(7)	0.8320(6)	0.0172(2)

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

Table S2. Selected Bond Lengths (Å) of $BaAg_2GeS_4$ and $BaAg_2SnS_4$.

$BaAg_2GeS_4$		$BaAg_2SnS_4$	
Ag–S	2.594(3)	Ag–S	2.491(5)
Ag–S	2.594(3)	Ag–S	2.491(5)
Ag–S	2.594(3)	Ag–S	2.786(5)
Ag–S	2.594(3)	Ag–S	2.786(5)
Ge–S	2.210(4)	Sn–S	2.388(5)
Ge–S	2.210(4)	Sn–S	2.388(5)
Ge–S	2.210(4)	Sn–S	2.388(5)
Ge–S	2.210(4)	Sn–S	2.388(5)
Ba–S	3.251(5)	Ba–S	3.292(6)
Ba–S	3.251(5)	Ba–S	3.292(6)
Ba–S	3.251(5)	Ba–S	3.292(6)
Ba–S	3.251(5)	Ba–S	3.292(6)
Ba–S	3.307(6)	Ba–S	3.337(6)
Ba–S	3.307(6)	Ba–S	3.337(6)
Ba–S	3.307(6)	Ba–S	3.337(6)
Ba–S	3.307(6)	Ba–S	3.337(6)