Supporting Information

New Strategy for Designing Promising Mid-Infrared Nonlinear Optical Materials: Narrowing Band Gap for Large Nonlinear Optical Efficiency and Reducing Thermal Effect for High Laser-induced Damage Threshold

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Table S1. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) of **1–4**.

Atom	*x*	*y*	*z*	*U*(eq)[a]	Occupancy	Wyckoff
			1			
Ga(1)	0.13321(9)	0.13559(5)	0.72040(17)	0.0223(3)	1	16b
Ge(1)	0	0	0.7426(2)	0.0245(4)	0.5	8a
Se(1)	-0.14470(11)	0.02067 (6)	0.5661(2)	0.0239(4)	0.5	16b
S(1)	-0.14470(11)	0.02067(6)	0.5661(2)	0.0239(4)	0.5	16b
Se(2)	0.05961(8)	0.13753(5)	0.42686(19)	0.0296(3)	1	16b
Se(3)	0.04403(9)	0.07747(5)	0.92845(18)	0.0315(3)	1	16b
Na(1)	-0.3310(7)	0.0441(4)	0.7460(11)	0.091(3)	1	16b
			2			
Ga(1)	-0.11864(6)	0.11439(3)	0.25668(11)	0.0177(2)	1	16b
Ge(1)	-0.2500	0.2500	0.27980(16)	0.0209(3)	0.5	8a
Se(1)	0.05799(6)	0.13732(4)	0.21497(12)	0.0237(2)	1	16b
Se(2)	-0.20837(6)	0.17221(3)	0.46353(11)	0.0242(2)	1	16b
Se(3)	-0.14668(6)	0.2035(3)	0.35311(13)	0.0278(2)	1	16b
Na(1)	-0.3347(4)	0.0455(2)	0.5311(7)	0.0843(18)	1	16b
			3			
Ga(1)	0.11684(5)	0.38593(3)	0.68892(9)	0.02013(19)	0.45	16b
Sn(1)	0.11684(5)	0.38593(3)	0.68892(9)	0.02013(19)	0.55	16b
Ga(2)	0.2500	0.2500	0.71598(15)	0.0176(3)	0.9	8a
Sn(2)	0.2500	0.2500	0.71598(15)	0.0176(3)	0.1	8a
Se(1)	0.14493(9)	0.48128(5)	0.78795(17)	0.0221(3)	0.5	16b
S(1)	0.14493(9)	0.48128(5)	0.78795(17)	0.0221(3)	0.5	16b
Se(2)	-0.05982(7)	0.36230(4)	0.63724(13)	0.0294(2)	1	16b
Se(3)	0.20674(7)	0.32756(4)	0.90405(13)	0.0287(2)	1	16b
Na(1)	-0.1725(5)	0.4558(3)	0.4666(8)	0.087(2)	1	16b
			4			
Ga(1)	0.11906(4)	0.11419(2)	0.34235(8)	0.01884(17)	0.5	16b
Sn(1)	0.11906(4)	0.11419(2)	0.34235(8)	0.01884(17)	0.5	16b
Ga(2)	0.2500	0.2500	0.31495(13)	0.0121(2)	0.5	8a
Se(1)	-0.05732(5)	0.13752(3)	0.39080(10)	0.0236(2)	1	16b
Se(2)	0.20921(5)	0.17211(3)	0.12949(9)	0.02181(19)	1	16b
Se(3)	0.14643(5)	0.01878(3)	0.24319(10)	0.0225(2)	1	16b

Na(1)	-0.1675(4)	0.0470(2)	0.5678(6)	0.0765(16)	1	16b

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

Table S2. Selected bond lengths (Å) for **1–4**.

1		**2**	
Ga(1)-S(1)/Se(1)	2.359(2)	Ga(1)-Se(1)	2.3791(12)
Ga(1)-Se(2)	2.378(2)	Ga(1)-Se(4)	2.3898(13)
Ga(1)-Se(3)	2.383(2)	Ga(1)-Se(2)	2.3927(13)
Ga(1)-Se(2)	2.406(2)	Ga(1)-Se(1)	2.4094(15)
Ge(1)-S(1)/Se(1)	2.352(2)	Ge(1)-Se(4)	2.3791(12)
Ge(1)-S(1)/Se(1)	2.352(2)	Ge(1)-Se(4)	2.3791(12)
Ge(1)-Se(3)	2.3744(19)	Ge(1)-Se(2)	2.3844(12)
Ge(1)-Se(3)	2.3744(19)	Ge(1)-Se(2)	2.3844(12)
Na(1)-S(1)/Se(1)	2.827(8)	Na(1)-Se(4)	2.854(5)
Na(1)-S(1)/Se(1)	2.871(8)	Na(1)-Se(4)	2.915(5)
Na(1)-Se(2)	2.958(9)	Na(1)-Se(1)	2.950(5)
Na(1)-Se(3)	2.993(9)	Na(1)-Se(2)	2.996(5)
Na(1)-Se(3)	3.482(10)	Na(1)-Se(2)	3.481(6)
3		**4**	
Ga(1)/Sn(1)-	2.4293(15)	Ga(1)/Sn(1)-Se(1)	2.4464(10)
Ga(1)/Sn(1)-Se(2)	2.4416(13)	Ga(1)/Sn(1)-Se(2)	2.4607(10)
Ga(1)/Sn(1)-Se(3)	2.4469(12)	Ga(1)/Sn(1)-Se(3)	2.4648(11)
Ga(1)/Sn(1)-Se(2)	2.4671(13)	Ga(1)/Sn(1)-Se(1)	2.4775(11)
Ga(2)/Sn(2)-	2.3845(14)	Ga(2)-Se(3)	2.4213(9)
Ga(2)/Sn(2)-	2.3845(14)	Ga(2)-Se(3)	2.4213(9)
Ga(2)/Sn(2)-Se(3)	2.4026(12)	Ga(2)-Se(2)	2.4234(10)
Ga(2)/Sn(1)-Se(3)	2.4026(12)	Ga(2)-Se(2)	2.4234(10)
Na(1)-S(1)/Se(1)	2.835(6)	Na(1)-Se(3)	2.900(5)
Na(1)-S(1)/Se(1)	2.869(6)	Na(1)-Se(3)	2.959(5)
Na(1)-Se(2)	2.982(2)	Na(1)-Se(1)	2.967(5)
Na(1)-Se(3)#9	3.015(6)	Na(1)-Se(2)	3.009(5)
Na(1)-Se(3)#8	3.494(8)	Na(1)-Se(2)	3.486(6)

Table S3. Thermal expansion coefficients α_L ($\times 10^{-5}$ K^{-1}) of *a*, *b* and *c* axis lengths and thermal expansion anisotropy of $LiInS_2$, $ZnGeP_2$, GaSe and $AgGaSe_2$.[1]

	$LiInS_2$	**$ZnGeP_2$**	**GaSe**	**$AgGaSe_2$**
a	1.61	1.59	0.92	-0.81
b	0.89			
c	0.66	1.75	1.09	1.98
δ	2.44	1.10	1.18	2.44
τ_p [ns]	10	30	30	35
LIDT[d] (GW/cm^2)	0.1 [a]	＞0.003[b]	0.03	0.011[c]

a： 10 Hz, bulk damage; *b*: 12.5 Hz; *c*: 1000 pulses;

1. D. N. Nikogosyan, *Nonlinear optical crystals: a complete survey*; Springer-Science: New York, 2005.

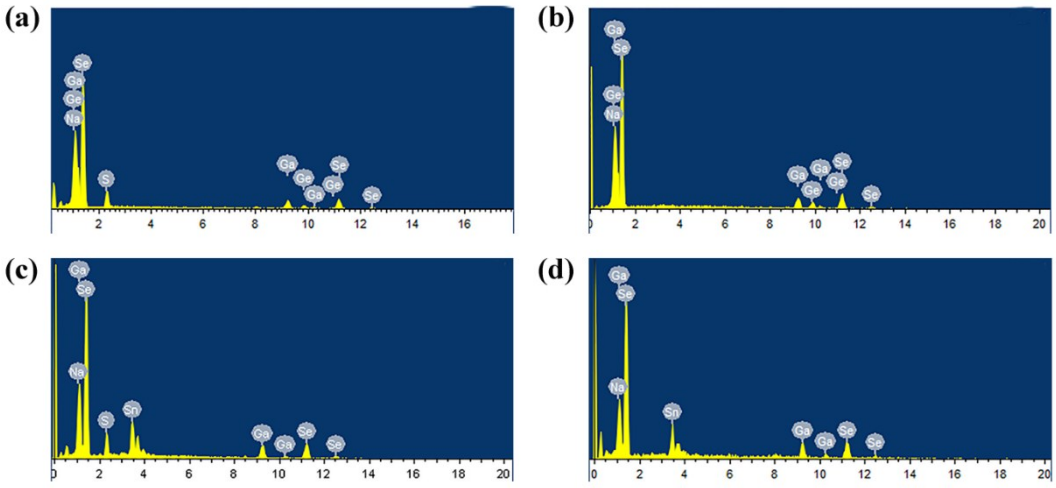

Fig. S1 EDS spectra of single-crystals for **1** (a) – **4** (d).

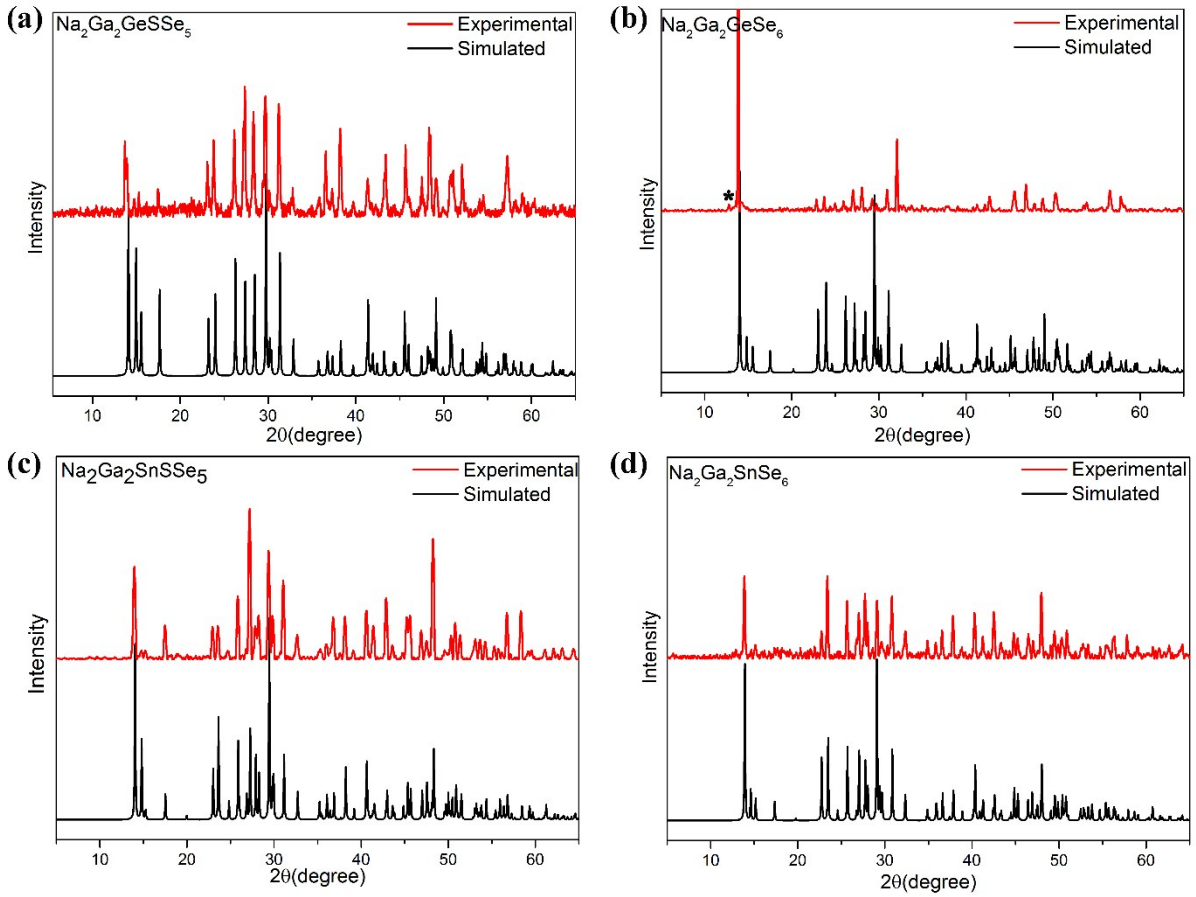

Fig. S2 Experimental (red) and simulated (black) powder X-ray diffraction (XRD) patterns of **1** (a) – **4** (d). The peak marked with * in (b) is from a small amount of $NaGa_3Se_5$ impurity.

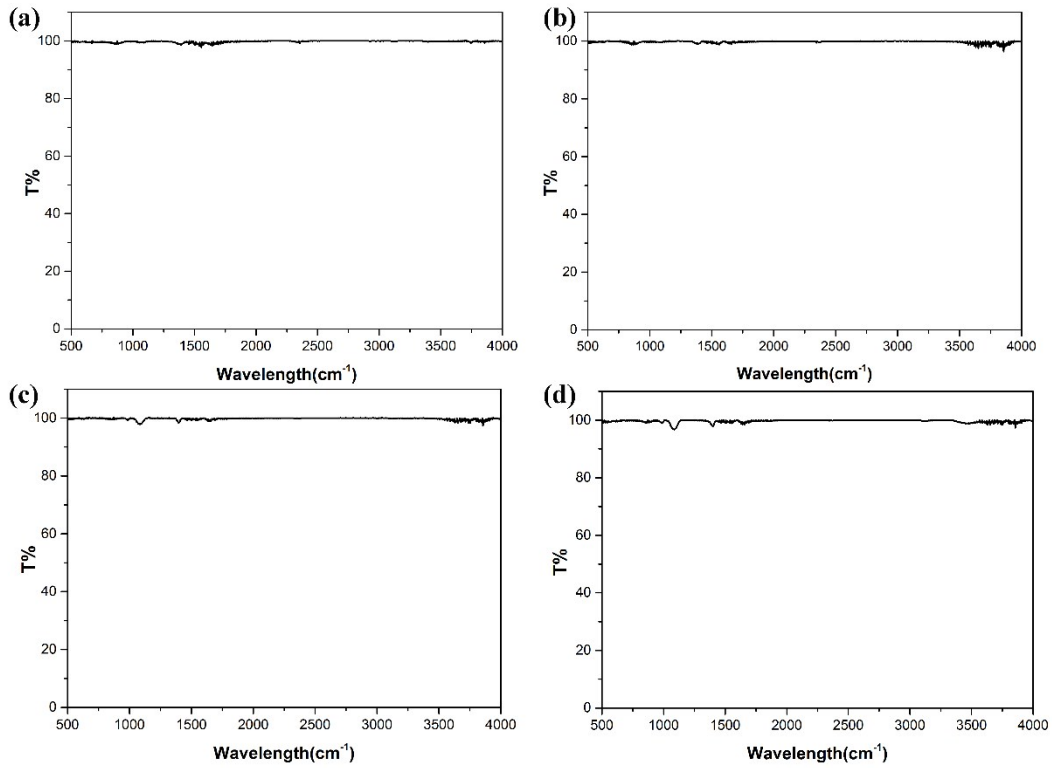

Fig. S3 IR spectra of **1** (a) – **4** (d).

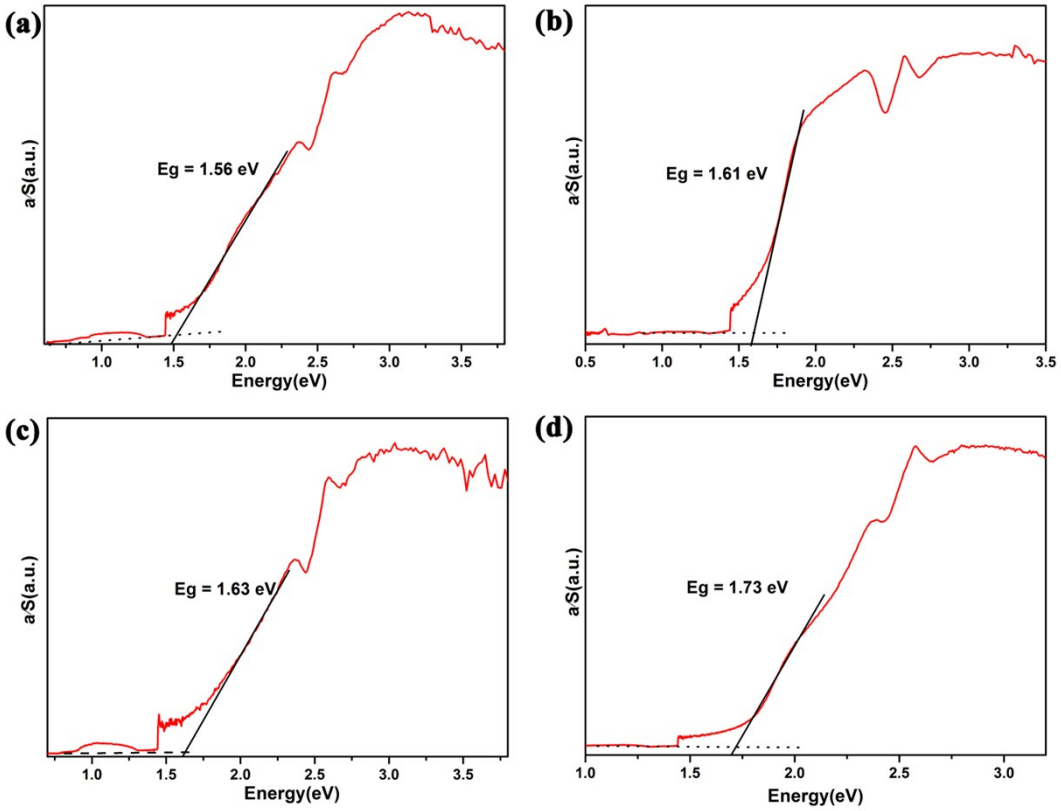

Fig. S4 UV–vis diffuse reflectance spectra of **1** (a) – **4** (d).

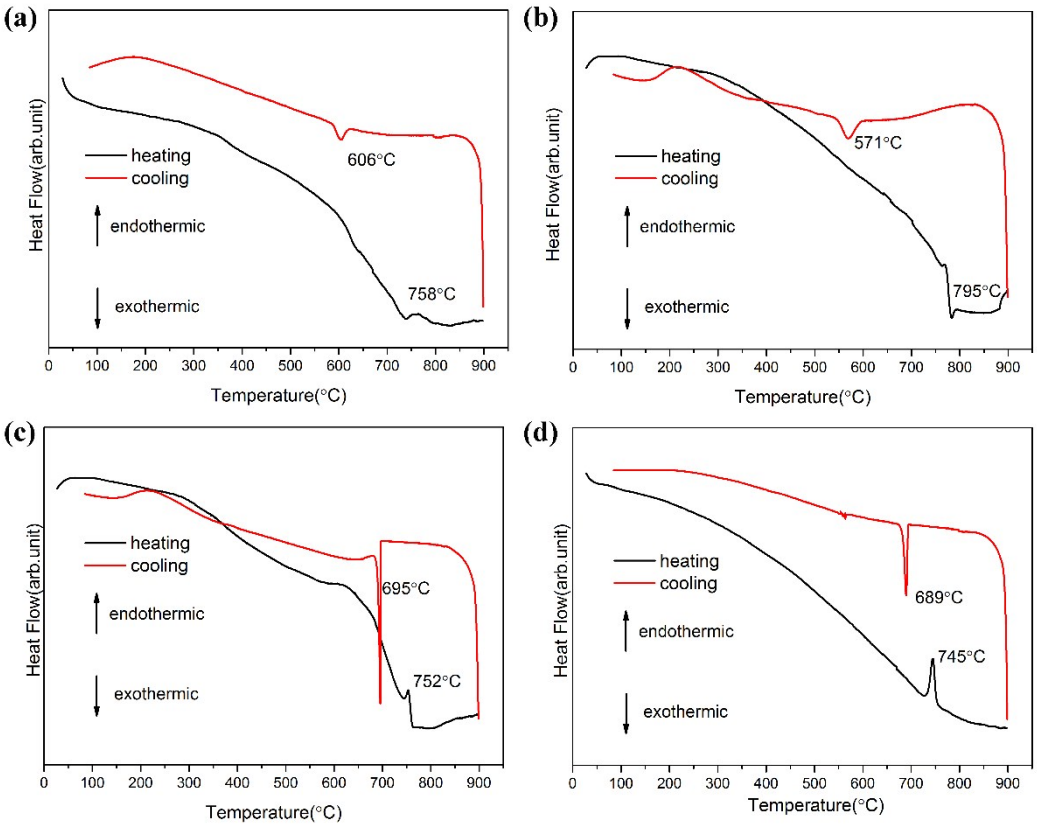

Fig. S5 DSC curves of **1** (a) – **4** (d).

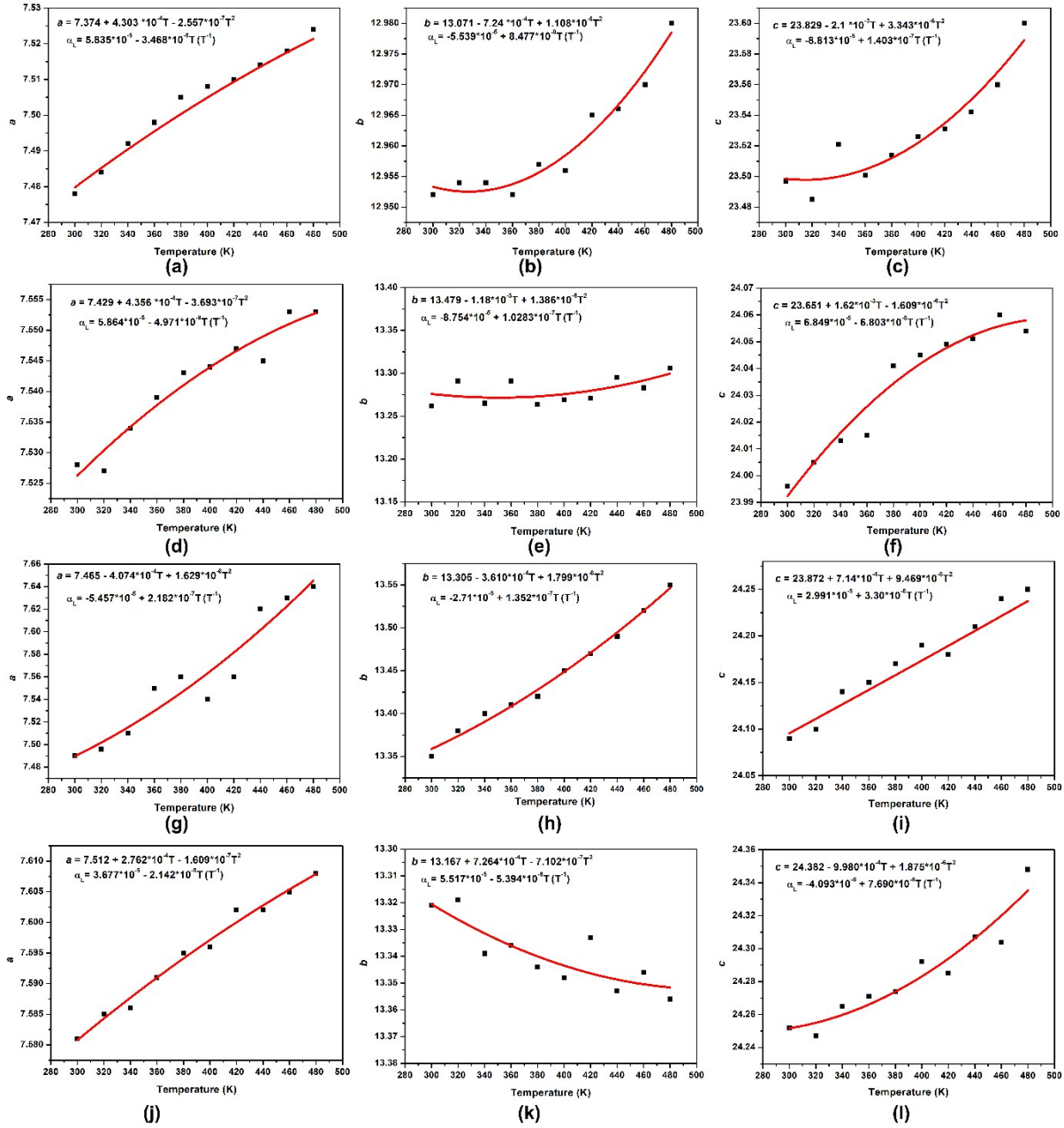

Fig. S6 Temperature dependence of the lattice parameters (lengths of *a*, *b* and *c* axises) of **1** (a, b, c), **2** (d, e, f), **3** (g, h, i) and **4** (j, k, l).

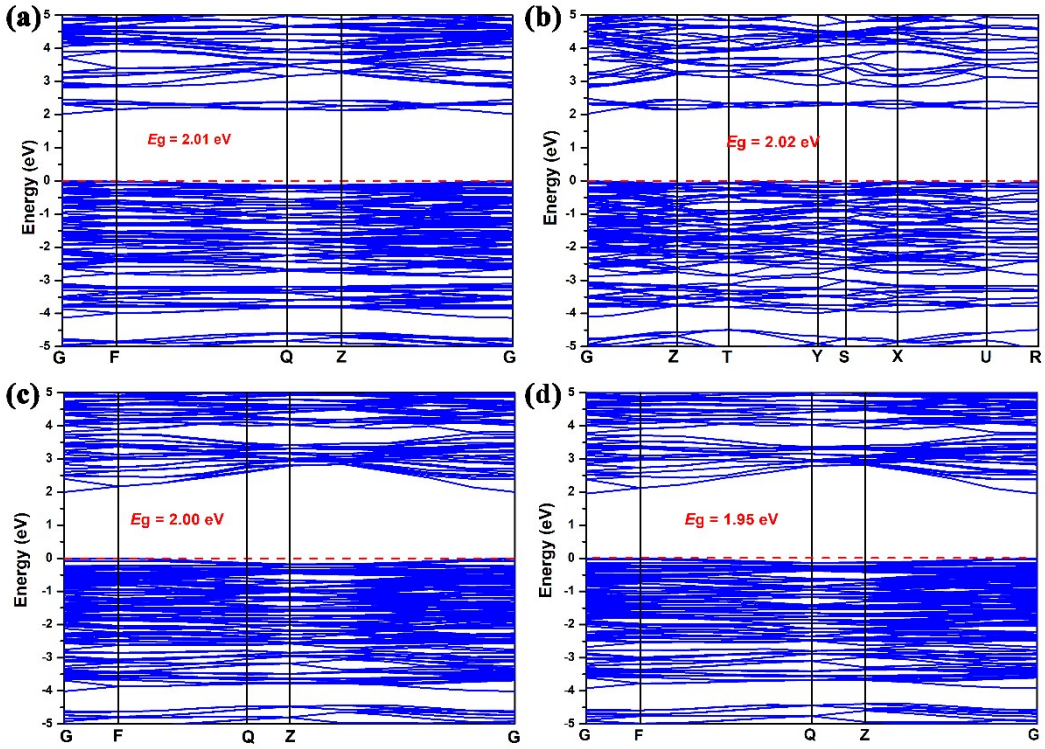

Fig. S7 Band structures of **1** (a) – **4** (d).

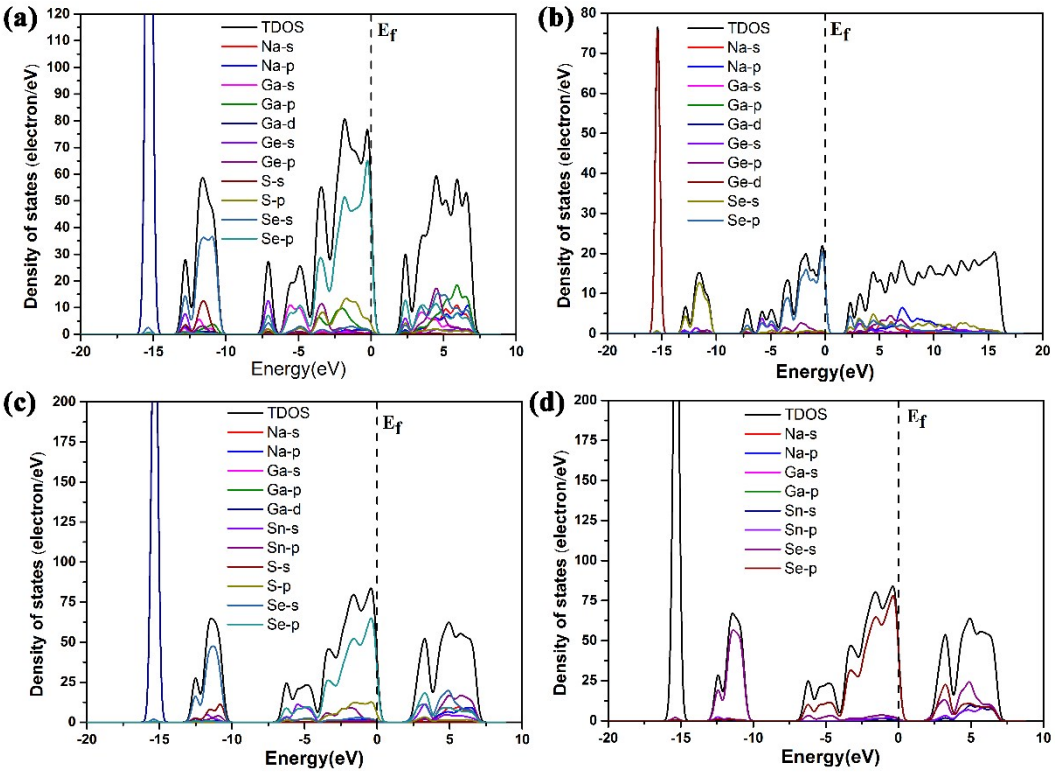

Fig. S8 Total and partial density of states of **1** (a) – **4** (d).

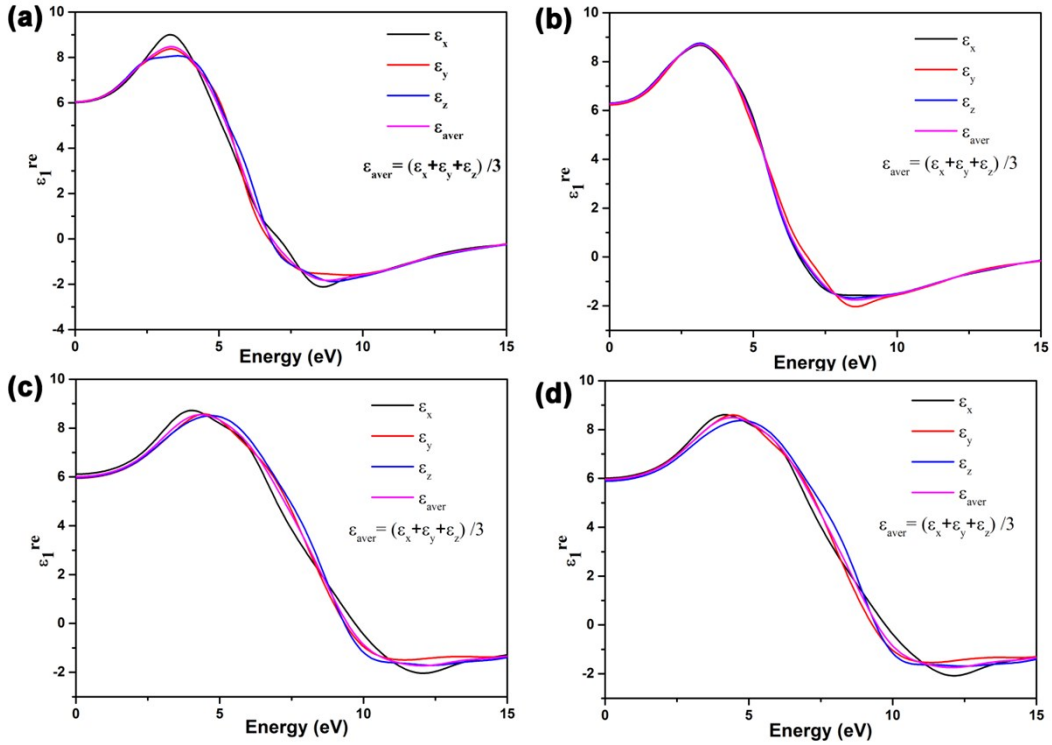

Fig. S9 Calculated real parts of optical dielectric functions of **1** (a) – **4** (d) in different polarization directions.

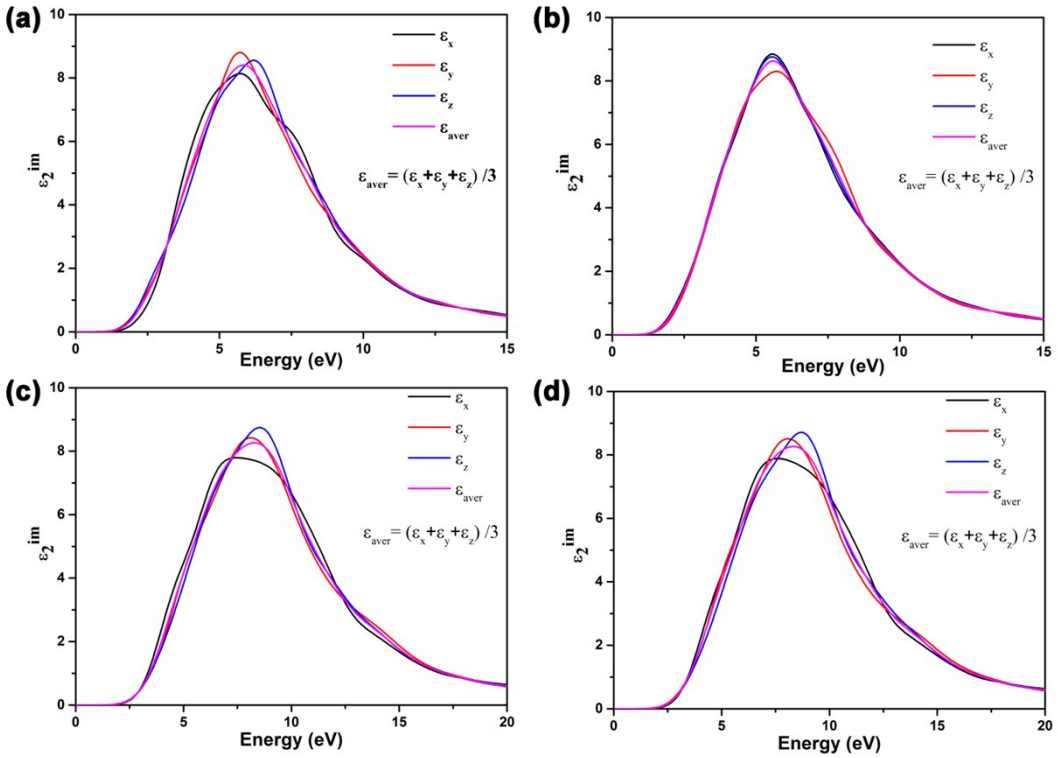

Fig. S10 Calculated imaginary parts of optical dielectric functions of **1** (a) – **4** (d) in different polarization directions.