Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Supporting Information

Table S1 Bond lengths (Å) and angles (°).

monoclinic Ga_2S_3[a]		cubic Ga_2S_3[b]	
Ga(1)-S(1)	2.200(2)	Ga(1)-S(1)	2.2547(6)
Ga(1)-S(2)#1	2.3102(19)	Ga(1)-S(1)#1	2.2547(6)
Ga(1)-S(3)	2.3207(17)	Ga(1)-S(1)#2	2.2547(6)
Ga(1)-S(2)	2.326(2)	Ga(1)-S(1)#3	2.2547(6)
Ga(2)-S(1)	2.196(2)	S(1)-Ga(1)#4	2.2547(6)
Ga(2)-S(2)#2	2.3111(18)	S(1)-Ga(1)#5	2.2547(6)
Ga(2)-S(3)#3	2.312(2)	S(1)-Ga(1)#6	2.2547(6)
Ga(2)-S(3)#4	2.3279(18)		
S(2)-Ga(1)#3	2.3102(19)		
S(2)-Ga(2)#5	2.3111(18)		
S(3)-Ga(2)#1	2.312(2)		
S(3)-Ga(2)#6	2.3279(18)		
S(1)-Ga(1)-S(2)#1	112.67(8)	S(1)-Ga(1)-S(1)#1	109.5
S(1)-Ga(1)-S(3)	111.40(7)	S(1)-Ga(1)-S(1)#2	109.5
S(2)#1-Ga(1)-S(3)	107.98(7)	S(1)#1-Ga(1)-S(1)#2	109.5
S(1)-Ga(1)-S(2)	115.70(8)	S(1)-Ga(1)-S(1)#3	109.5
S(2)#1-Ga(1)-S(2)	106.36(7)	S(1)#1-Ga(1)-S(1)#3	109.5
S(3)-Ga(1)-S(2)	101.94(7)	S(1)#2-Ga(1)-S(1)#3	109.5
S(1)-Ga(2)-S(2)#2	110.96(7)	Ga(1)-S(1)-Ga(1)#4	109.5
S(1)-Ga(2)-S(3)#3	114.69(8)	Ga(1)-S(1)-Ga(1)#5	109.5
S(2)#2-Ga(2)-S(3)#3	109.26(8)	Ga(1)#4-S(1)-Ga(1)#5	109.5
S(1)-Ga(2)-S(3)#4	110.48(8)	Ga(1)-S(1)-Ga(1)#6	109.5
S(2)#2-Ga(2)-S(3)#4	106.01(7)	Ga(1)#4-S(1)-Ga(1)#6	109.5
S(3)#3-Ga(2)-S(3)#4	104.94(7)	Ga(1)#5-S(1)-Ga(1)#6	109.5

Ga(2)-S(1)-Ga(1)	105.78(9)
Ga(1)#3-S(2)-Ga(2)#5	109.35(7)
Ga(1)#3-S(2)-Ga(1)	102.74(7)
Ga(2)#5-S(2)-Ga(1)	109.38(8)
Ga(2)#1-S(3)-Ga(1)	103.93(7)
Ga(2)#1-S(3)-Ga(2)#6	107.07(8)
Ga(1)-S(3)-Ga(2)#6	111.36(8)

[a]Symmetry codes: (#1) x,-y,z+1/2; (#2) x+1/2,-y-1/2,z+1/2; (#3) x,-y,z-1/2; (#4) x,y-1,z; (#5) x-1/2,-y-1/2,z-1/2; (#6) x,y+1,z.

[b]Symmetry codes: (#1) x-1/2,y-1/2,z; (#2) x,y-1/2,z-1/2; (#3) x-1/2,y,z-1/2; (#4) x+1/2,y+1/2,z; (#5) x,y+1/2,z+1/2; (#6) x+1/2,y,z+1/2.

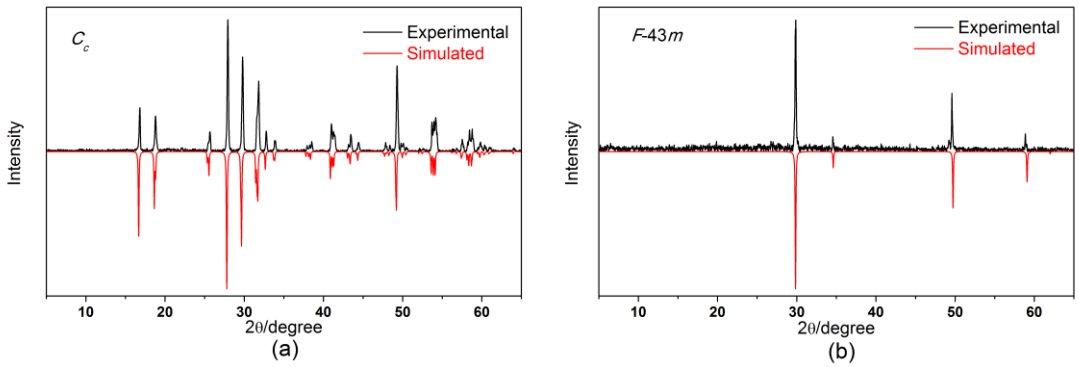

Fig. S1 The experimental and simulated X-ray powder diffraction patterns of the monoclinic (a) and cubic Ga_2S_3 (b).

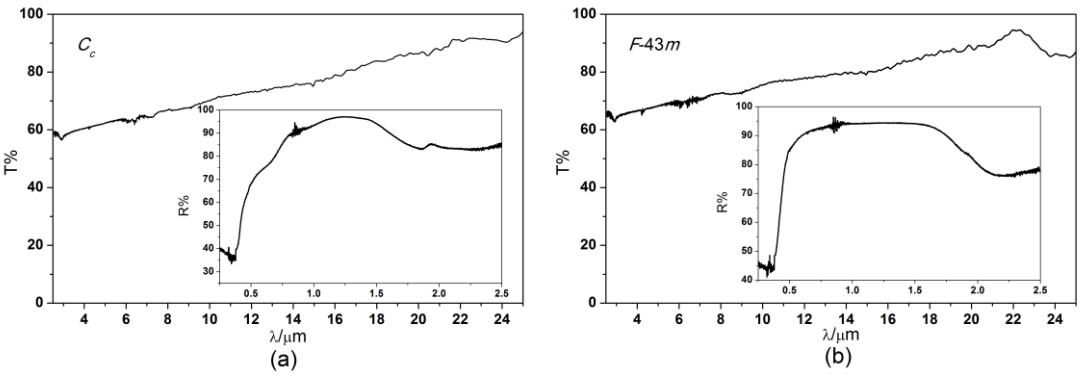

Fig. S2 UV-Vis-NIR diffuse reflectance spectra (inset panel) and IR transmission spectra of monoclinic (a) and cubic Ga_2S_3 (b).

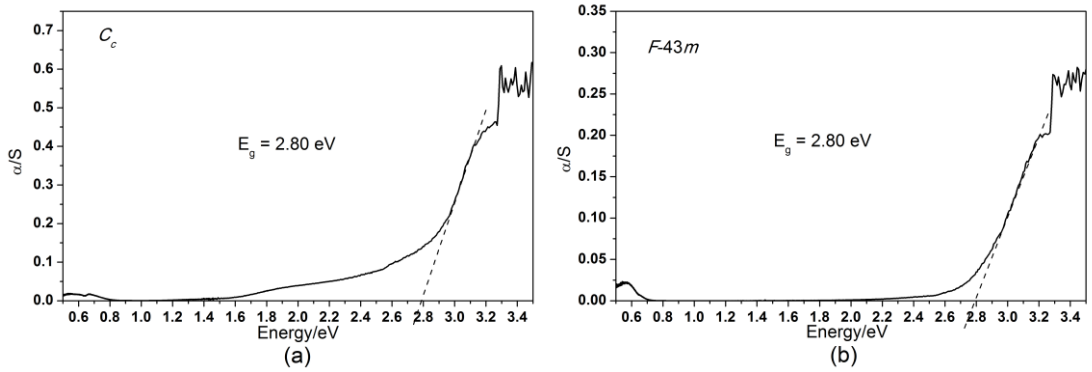

Fig. S3 Optical diffuse reflectance spectra of the monoclinic (a) and cubic Ga_2S_3 (b).

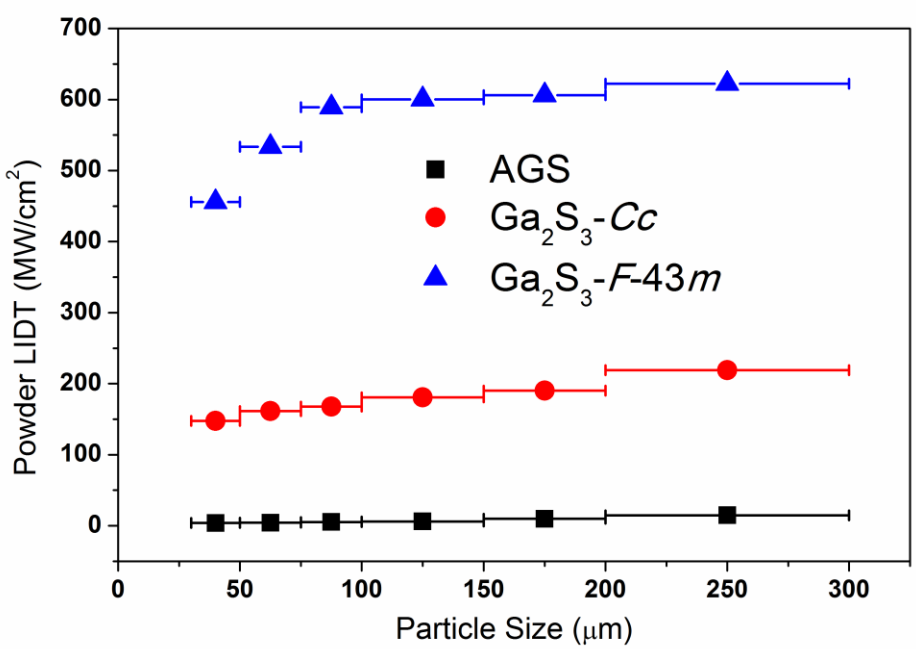

Fig. S4 Particle size dependences of powder LIDT values for AGS, monoclinic and cubic Ga_2S_3.

The dependences of powder LIDT values versus particle size for AGS, monoclinic and cubic Ga_2S_3 were investigated by our method. The experimental results were summarized and plotted in **Fig. S4**.

Firstly, the powder LIDT values increase with the particle size for these three compounds similarly, which could be explained by the decrease of defects per unit area as the increase of the particle size. It could be deduced that the phenomenon, which the powder LIDT values increase as the particle size, would be observed for all

compounds. Secondly, the powder LIDT values of monoclinic and cubic Ga_2S_3 are always larger than those of the corresponding AGS with the same particle size. Those situations also reflect the accuracy and reliability of our method and prove that the method is an effective and semiquantitative method to evaluate the powder LIDT values for new NLO compounds.

Considering that the samples synthesized by solid-state reactions are mainly distributed in the particle size range of 75-150 μm, the particle size range of 75-150 μm is preferred to be adopted for comparatively parallel contrast between our title compounds and AGS, which also simplifies the test method.

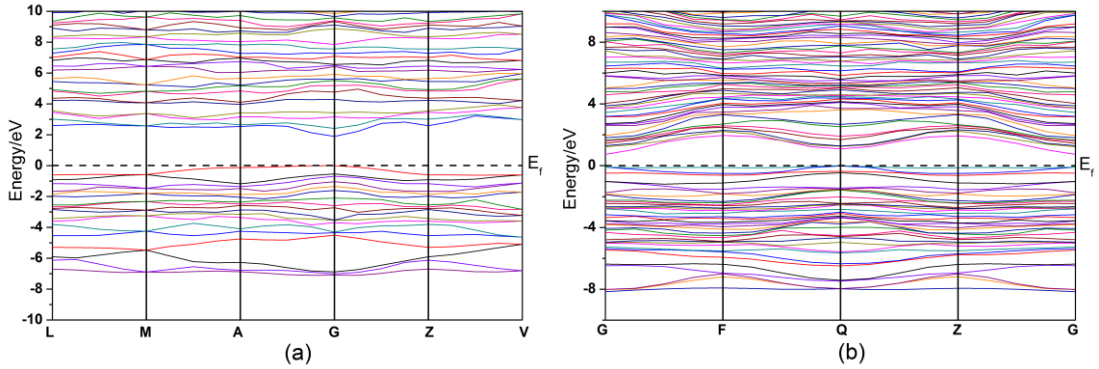

Fig. S5 The band structures of monoclinic (a) and cubic Ga_2S_3 (b).

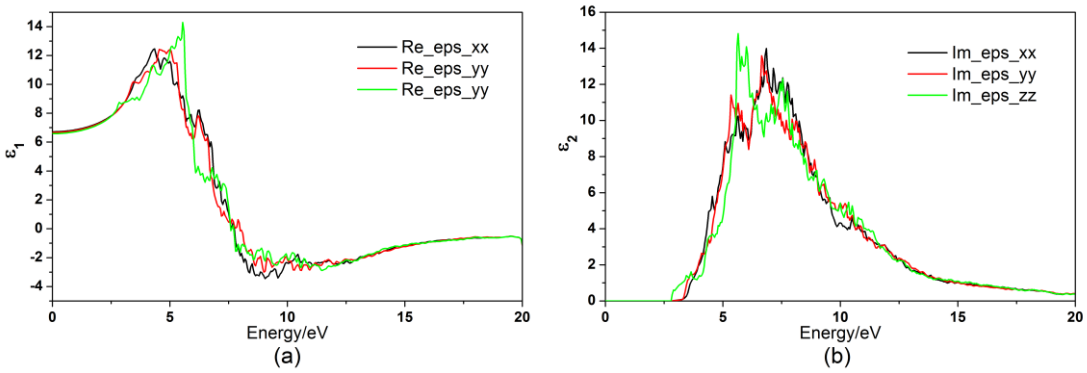

Fig. S6 Energy dependences of the real part ε_1 (a) and the imaginary part ε_2 (b) of monoclinic Ga_2S_3.

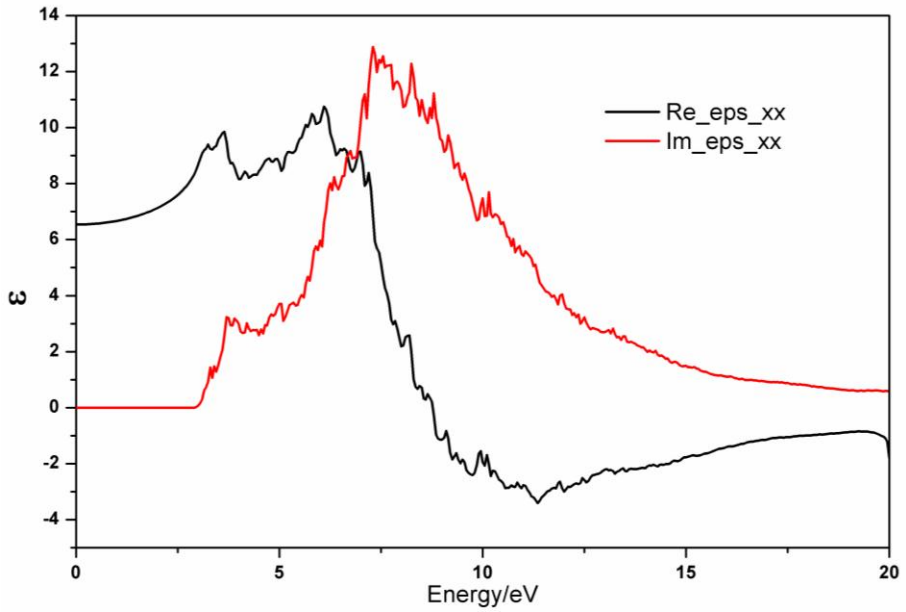

Fig. S7 Energy dependences of the real part ε_1 and the imaginary part ε_2 of cubic Ga_2S_3.

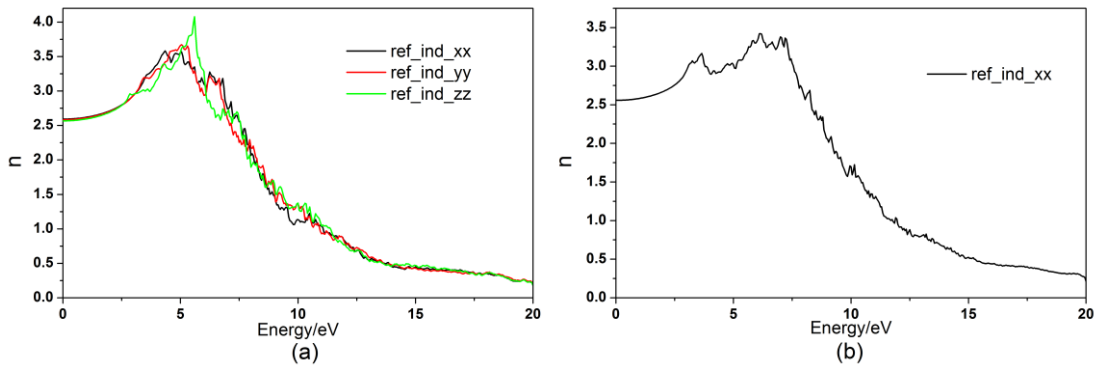

Fig. S8 Variations of the calculated refractive index n of monoclinic (a) and cubic Ga_2S_3 (b).

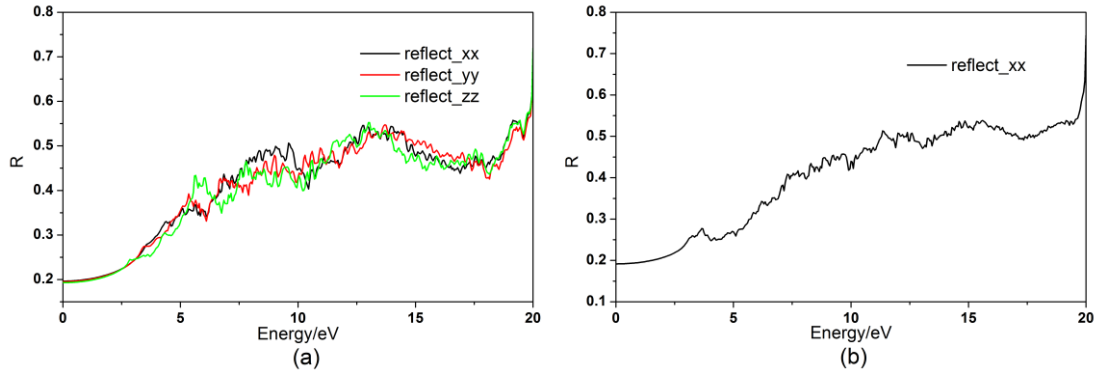

Fig. S9 Calculated reflectivity R of monoclinic (a) and cubic Ga_2S_3 (b).

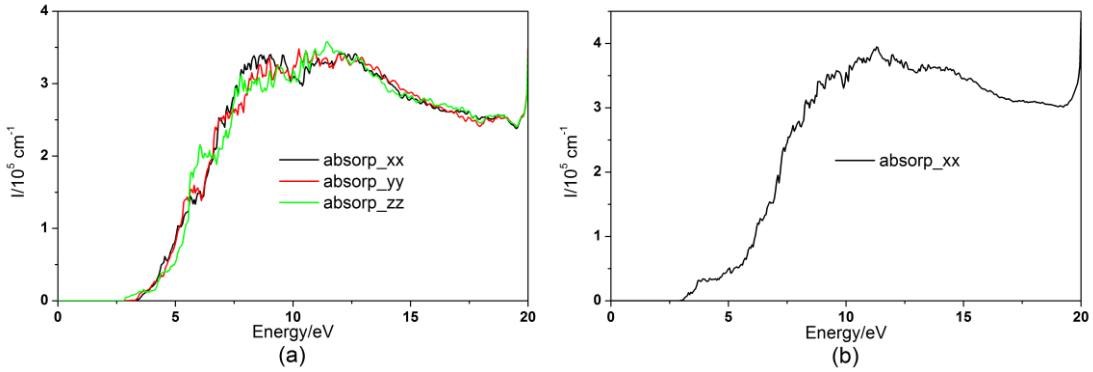

Fig. S10 Calculated absorption coefficient *I* of monoclinic (a) and cubic Ga_2S_3 (b).

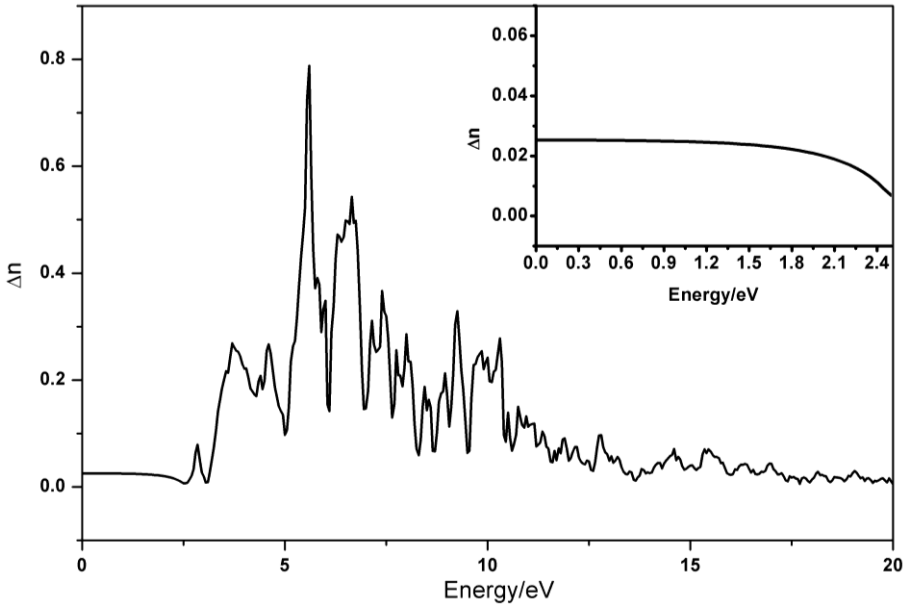

Fig. S11 Calculated birefringence Δn of monoclinic Ga_2S_3.