Electronic Supplementary Information

Combined experimental and theoretical investigations of Ba_3GaS_4I: interesting structure transformation originated from the halogen substitution

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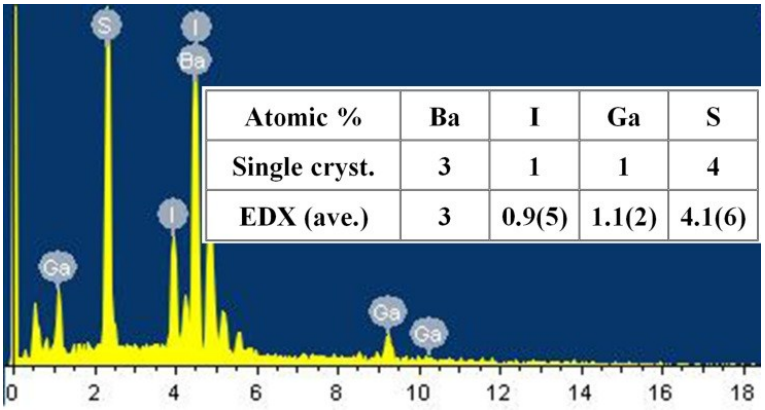

Atomic %	Ba	I	Ga	S
Single cryst.	3	1	1	4
EDX (ave.)	3	0.9(5)	1.1(2)	4.1(6)

Figure S1. EDX results of Ba_3GaS_4I.

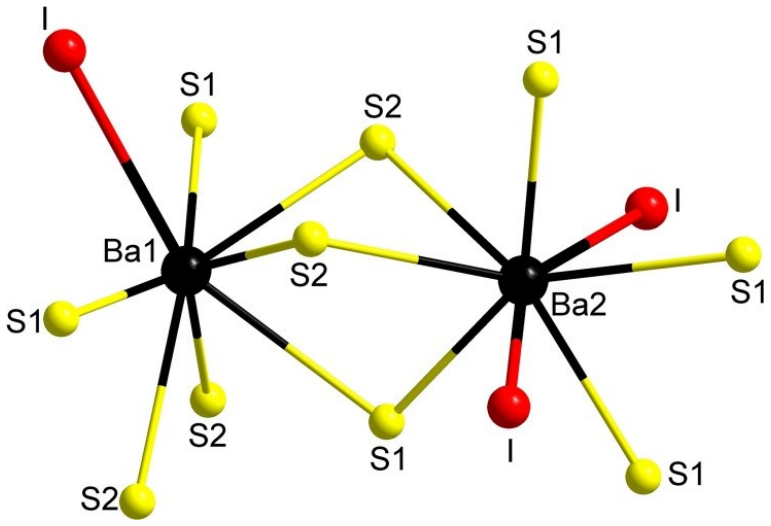

Figure S2. The coordination geometries of Ba atoms in Ba_3GaS_4I.

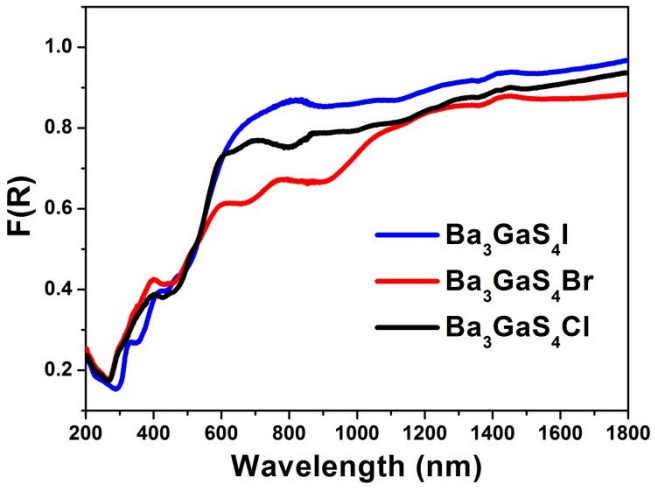

Figure S3. UV−vis diffuse reflectance spectra for Ba_3GaS_4X (X = Cl, Br, I).

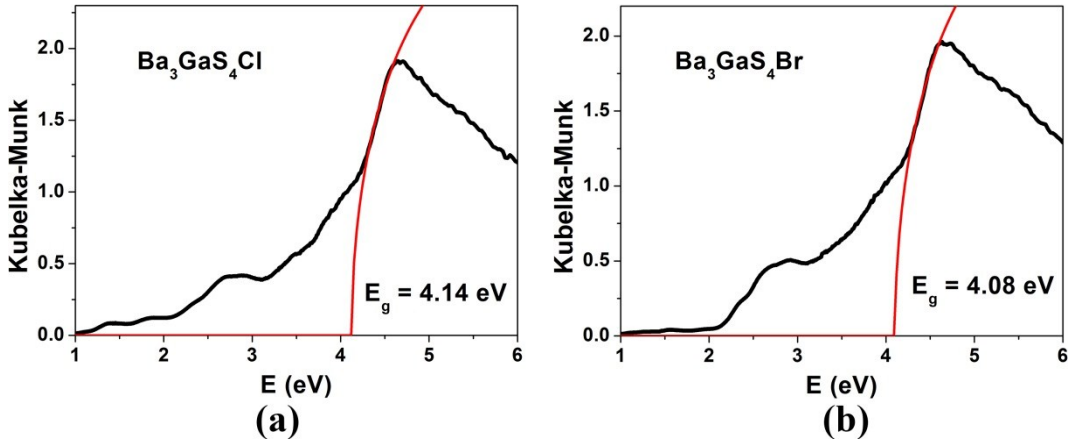

Figure S4. The experimental band gap of Ba_3GaS_4X (X = Cl, Br) were determined by fitting the absorption edge with Tauc's function describing a direct semiconductor.

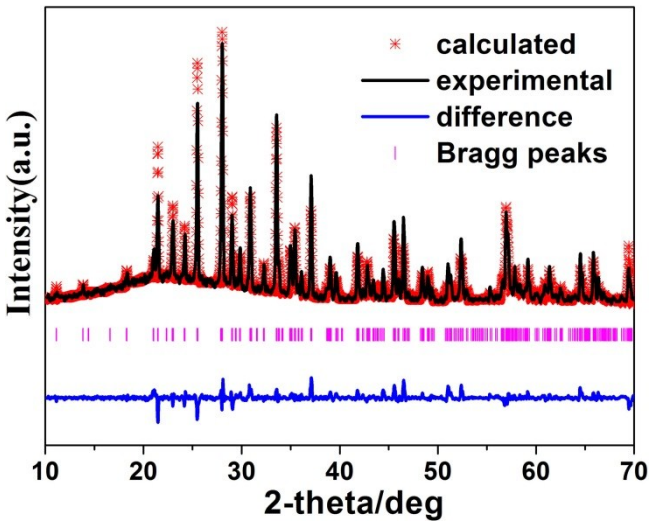

Figure S5. Experimental, calculated, positions of the Bragg peaks and difference results of powder XRD refined by General Structure Analysis System (GSAS) for Ba_3GaS_4I after DTA.

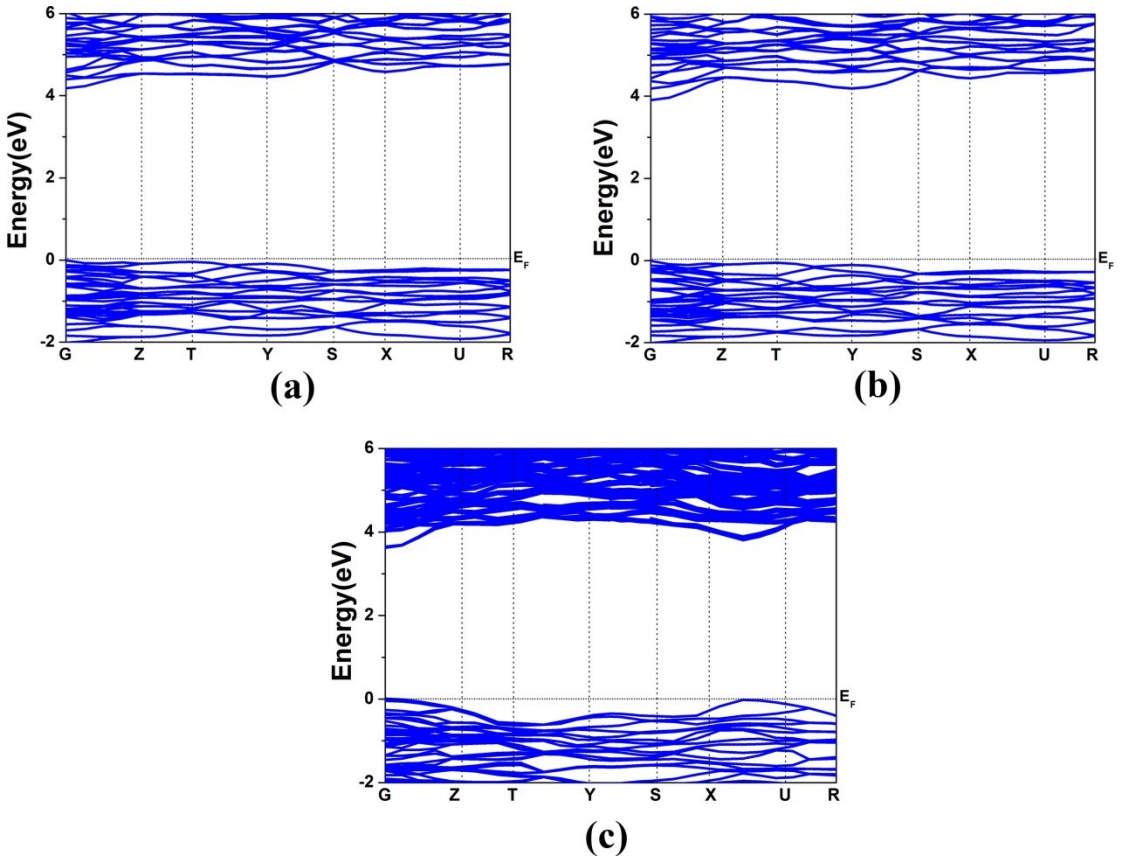

Figure S6. Calculated band structures of Ba_3GaS_4X (X = Cl, Br and I).

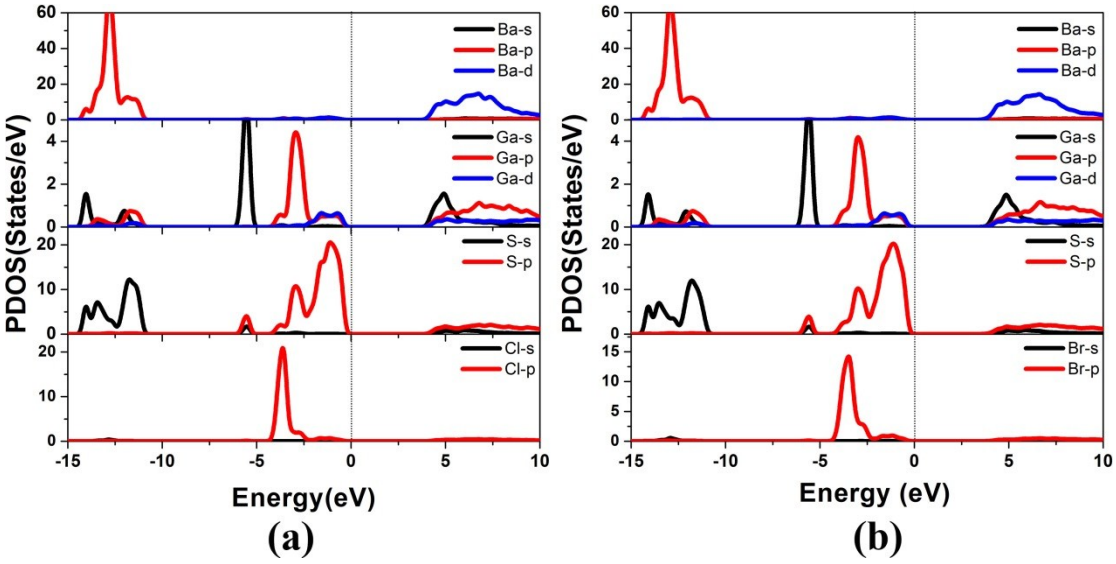

Figure S7. Calculated PDOS of Ba_3GaS_4X (X = Cl, Br).

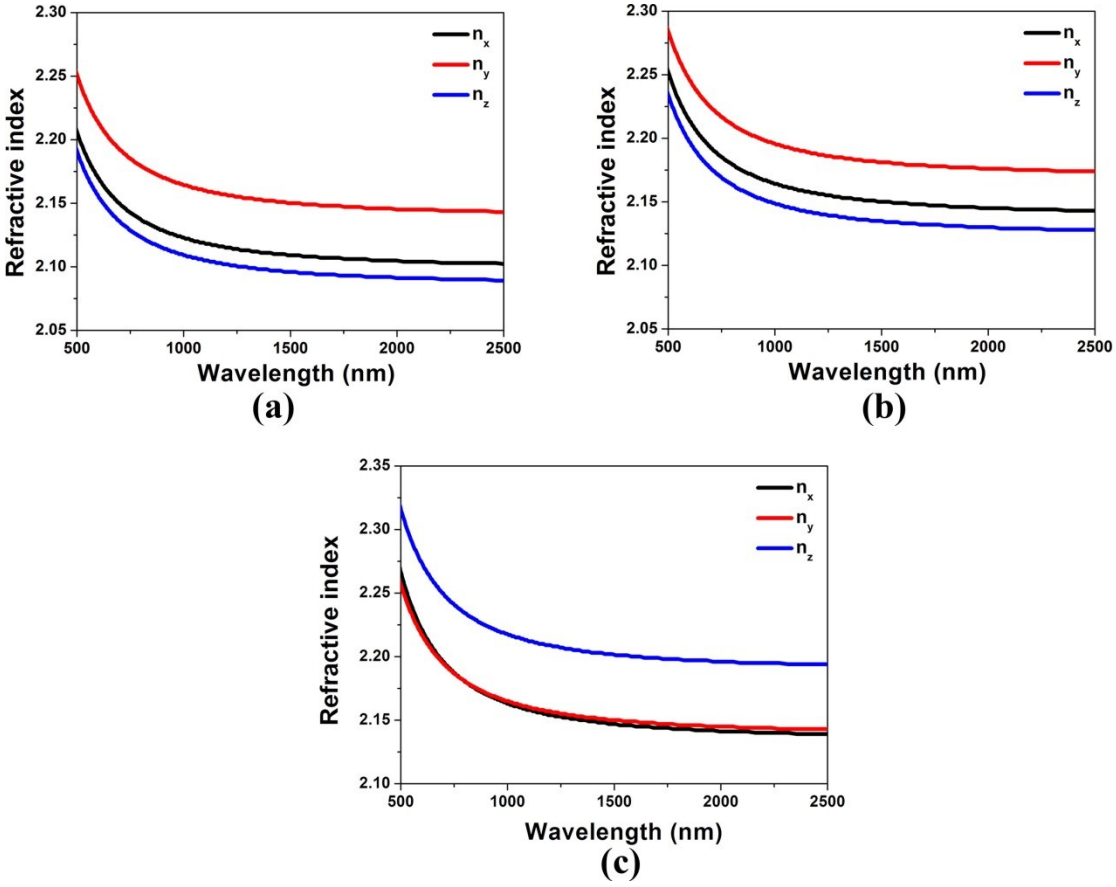

Figure S8. Calculated refractive indices of Ba_3GaS_4X (X = Cl, Br and I).

Table S1. Selected Ga–S distances (Å) for Ba_3GaS_4X (X = Cl, Br, I).

	Ba_3GaS_4Cl[1]	Ba_3GaS_4Br[1]	Ba_3GaS_4I	
space group	*Pnma*	*Pnma*	*Cmcm*	
Ga–S1×2	2.2321(8)	2.231(3)	Ga–S1×2	2.2239(12)
Ga–S2	2.2682(12)	2.276(4)	Ga–S2×2	2.2750(11)
Ga–S3	2.2655(12)	2.258(4)		
d_{ave}(Ga–S)	**2.2495**	**2.249**		**2.2495**

Table S2. Selected ∠S–Ga–S bond angle (°) for Ba_3GaS_4X (X = Cl, Br, I).

	Ba_3GaS_4Cl[1]	Ba_3GaS_4Br[1]	Ba_3GaS_4I	
∠S1–Ga–S1	119.54(5)	116.28(17)	∠S1–Ga–S1	118.20(6)
∠S1–Ga–S3	107.25(3)	108.02(10)	∠S1–Ga–S2	108.42(2)
∠S1–Ga–S3	107.25(3)	108.02(10)	∠S1–Ga–S2	108.42(2)
∠S1–Ga–S2	105.75(3)	106.88(10)	∠S1–Ga–S2	108.42(2)
∠S1–Ga–S2	105.75(3)	106.88(10)	∠S1–Ga–S2	108.42(2)
∠S3–Ga–S2	111.30(4)	110.76(15)	∠S1–Ga–S2	104.07(6)
Σ	**23.78**	**16.18**		**18.33**

REFERENCES

[1] Feng, K.; Yin, W.; Lin, Z.; Yao, J.; Wu, Y. *Inorg. Chem.* **2013**, *52*, 11503−11508.