Electronic Supplementary Information:

Design and synthesis of Ba_3SiSe_5 with suitable birefringence modulated via M^{IV} atoms in Ba-M^{IV}-Q (M^{IV} = Si, Ge; Q = S, Se) system

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Contents

Theoretical Calculations of other compounds in Ba-M^{IV}-Q (M^{IV} = Si, Ge; Q = S, Se) system. Utilized the plane wave pseudopotential method implemented in the CASTEP package, the first principle calculation of other compounds in Ba-M^{IV}-Q (M^{IV} = Si, Ge; Q = S, Se) system based on the density functional theory (DFT) were carried out. The exchange-correlation functional was executed by Perdew-Burke-Ernzerh (PBE) of functions within the generalized gradient approximation (GGA). The norm-conserving pseudopotentials (NCP) were selected for structural optimization and calculating the properties of electronic and optical. The following electronic configurations were treated as: Ba $5s^25p^66s^2$, Si $3s^23p^2$, Se $4s^24p^4$, Ge $4s^24p^2$, S $3s^23p^4$, the cutoff energy was set to 720 eV for Ba_3SiS_5, Ba_3GeS_5 Ba_2GeS_4 and Ba_2SiS_4, 440 eV for Ba_2GeSe_4 and Ba_2SiSe_4, respectively. Furthermore, to reach the convergence of this calculations, the Brillouin zone comprised of Monkhorst-Pack *k*-point sampling with a separation was set as: 3 × 3 × 3 and 0.03 $Å^{-1}$ for Ba_3SiS_5 and Ba_3GeS_5, 4 × 5 × 3 and 0.03 $Å^{-1}$ for Ba_2GeS_4 and Ba_2SiS_4, 4 × 4 × 3 and 0.04 $Å^{-1}$ for Ba_2GeSe_4 and Ba_2SiSe_4, respectively. The other calculation parameters and convergent criteria were employed as the default values of the CASTEP code.

Table S1 Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for Ba_3SiSe_5.

Atom	Wckoff position	*x*	*y*	*z*	Ueq (Å^2)
Ba1	4c	4778(1)	7500	8867(1)	14(1)
Ba2	8d	6812(1)	4822(1)	5751(1)	21(1)
Se1	4c	2212(1)	2500	6516(2)	13(1)
Se2	4c	4969(1)	2500	4818(2)	14(1)
Se3	8d	4454(1)	4376(1)	8199(1)	16(1)
Se4	4c	7344(1)	7500	8150(2)	21(1)
Si	4c	4011(3)	2500	6941(4)	7(1)

Table S2 Interatomic distance (Å) and angles in Ba_3SiSe_5.

Atoms	Interatomic Distance (Å) or Angles (deg)	Atoms	Interatomic Distance (Å) or Angles (deg)
Ba1-Se3(×2)	3.1727(12)	Ba2-Se3	3.6885(13)
Ba1-Se3(×2)	3.3556(14)	Ba2-Se4	3.4354(14)
Ba1-Se4	3.2545(19)	Ba2-Se4	3.4733(13)
Ba1-Se4	3.5249(18)	Si-Se1	2.269(4)
Ba1-Se2	3.3154(17)	Si-Se3(×2)	2.239(2)
Ba1-Se1	3.4287(17)	Si-Se2	2.244(4)
Ba2-Se1	3.3923(13)	Se3-Si-Se3	111.88(16)
Ba2-Se1	3.5511(12)	Se3-Si-Se2(×2)	107.18(11)
Ba2-Se2	3.4905(12)	Se3-Si-Se1(×2)	109.09(11)
Ba2-Se2	3.3502(13)	Se2-Si-Se1	112.44(15)
Ba2-Se3	3.4449(14)		

Table S3 Mulliken bond populations in Ba_3SiSe_5.

Compounds	Bond	Population
Ba_3SiSe_5	Ba-Se	0.03-0.18
	Si-Se	0.38-0.46

Table S4 Crystallographic structure data of the Ba-M^{IV}-Q (M^{IV} = Si, Ge; Q = S, Se) system.

Compounds	Space group	Band gap (eV)		Birefringence	Volume ($Å^{-3}$)	Unit cell dimensions (Å)
		GGA	HSE06			
Ba_3SiSe_5	*Pnma*	2.30	3.07	0.044	1101.4	12.436(3), 9.889(2), 8.9564(19)
Ba_3SiS_5[1]	*Pnma*	2.83	3.60	0.036	987.67	12.121(10), 9.527(8), 8.553(8)
Ba_3GeS_5[2]	*Pnma*	2.20	3.08	0.050	989.62	12.053(9), 9.550(7), 8.600(6)
Ba_2GeS_4[3]	*Pnma*	2.40	3.37	0.078	754.74	8.983(11), 6.875(9), 12.221(16)
Ba_2SiS_4[4]	*Pnma*	3.05	4.04	0.051	727.44	8.930(9), 6.782(4), 12.011(8)
Ba_2GeSe_4[5]	*P2/m*	1.71	2.60	0.067	430.11	7.000(4), 7.094(4), 9.174(6), β = 109.14(10)
Ba_2SiSe_4[6]	*P2/m*	2.43	3.25	0.060	419.18	9.184(5), 7.033(3), 6.872(3), β = 109.2(1)
$Ba_2Ge_2Se_5$[7]	*Pnma*	/	/	/	1058.32	12.594(3), 9.174(2), 9.160(2)
$Ba_2Ge_4S_{10}$[8]	*Fd3-m*	/	/	/	3307.28	14.899(2), 14.899(2), 14.899(2)
$Ba_2Ge_2S_6$[9]	*P2/c*	/	/	/	1070.72	15.376(6), 5.761(17), 13.420(4), β = 115.72(2)

Table S5 Bond valence sums in Ba_3SiSe_5, Ba_3SiS_5[1] and Ba_3GeS_5[2].

Ba_3SiSe_5		Ba_3SiS_5		Ba_3GeS_5	
Ba1	2.5	Ba1	1.8	Ba1	1.7
Ba2	1.6	Ba2	2.5	Ba2	2.6
Si	4.1	Si	3.7	Ge	4.3
Se1	2.0	S1	2.1	S1	2.2
Se2	2.3	S2	2.2	S2	2.3
Se3	2.2	S3	1.3	S3	2.1
Se4	1.4	S4	2.0	S4	1.4

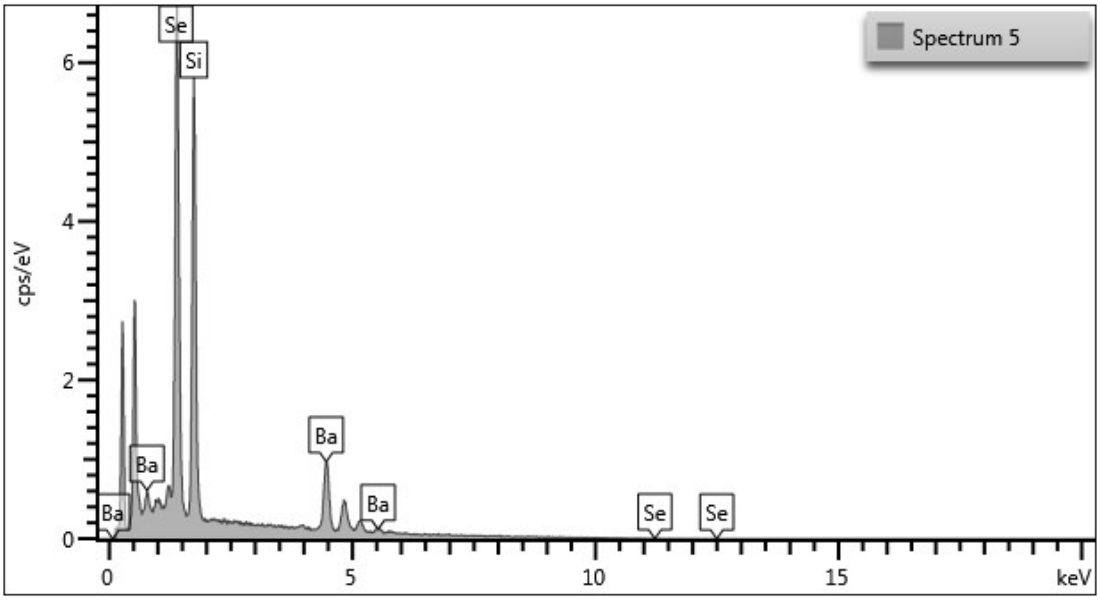

Fig. S1 The energy dispersive X-ray spectroscope (EDX) pattern.

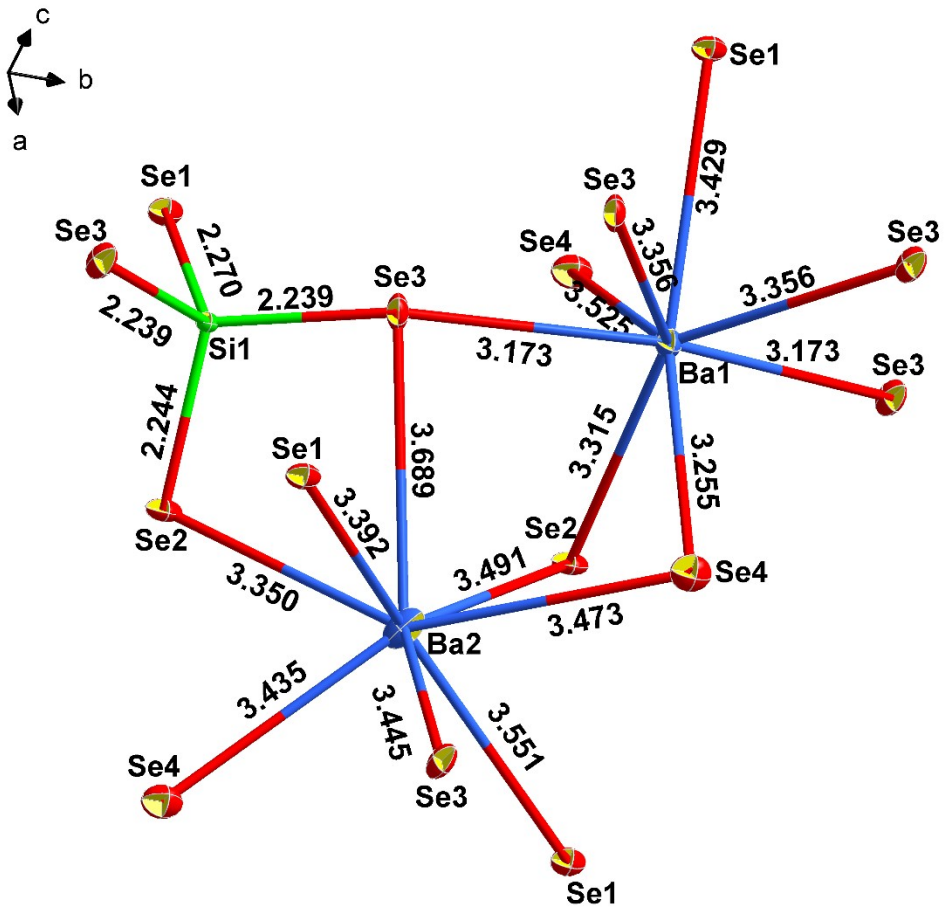

Fig. S2 Asymmetric unit and selected symmetry-equivalent atoms in Ba_3SiSe_5.

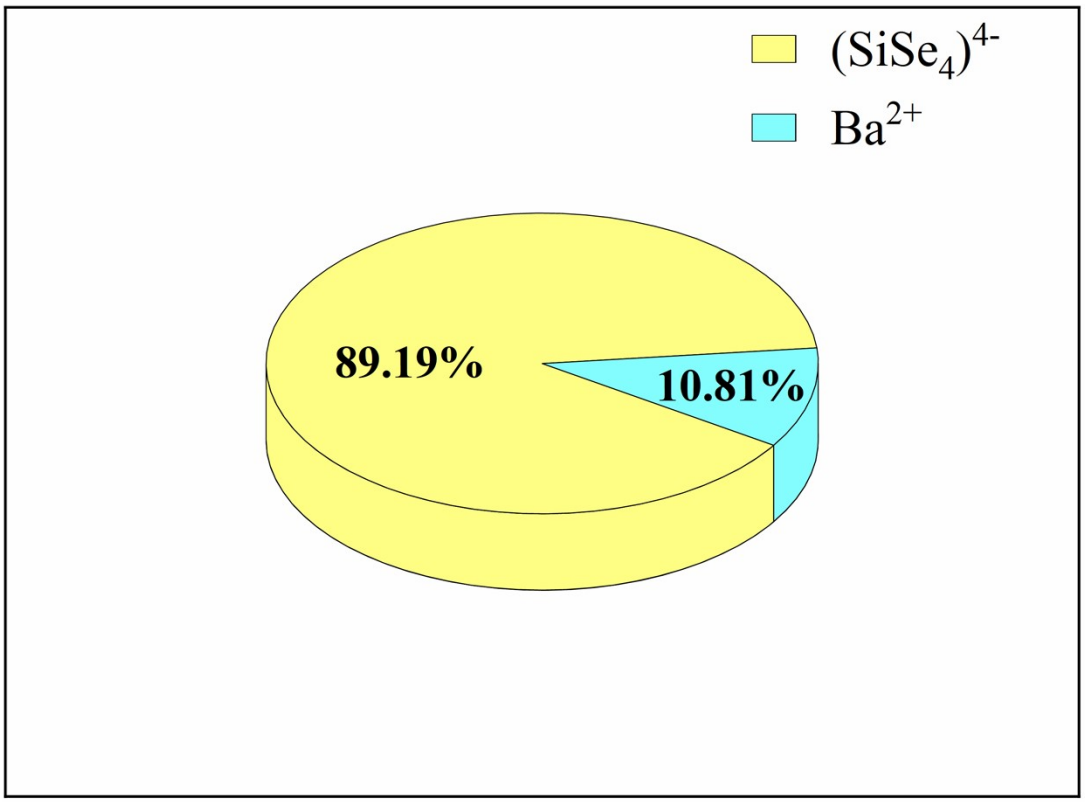

Fig. S3 The real-space atom-cutting analysis of Ba_3SiSe_5.

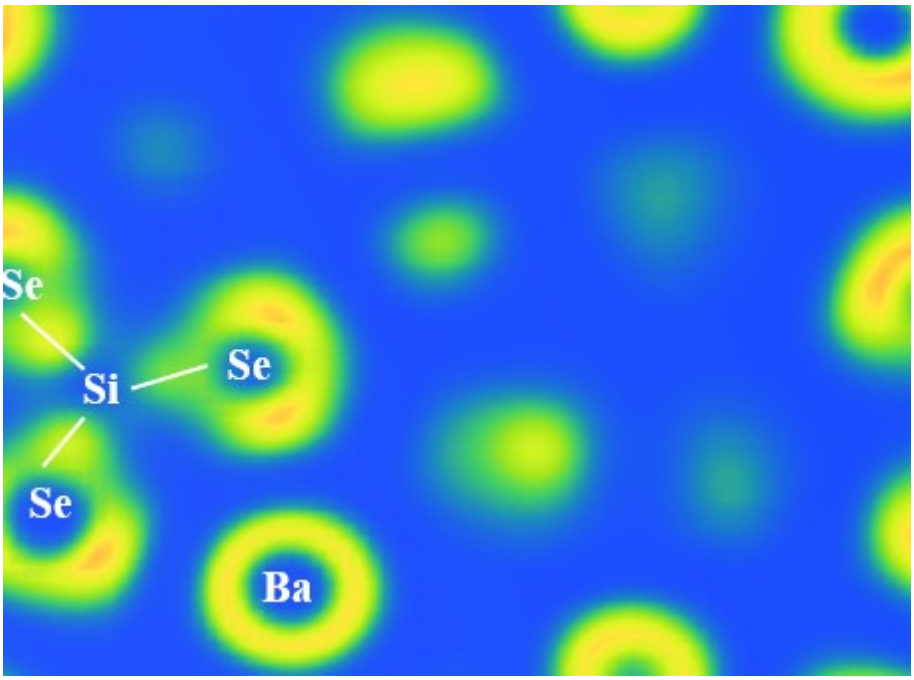

Fig. S4 Electron localization function (ELF) diagram of Ba_3SiSe_5.

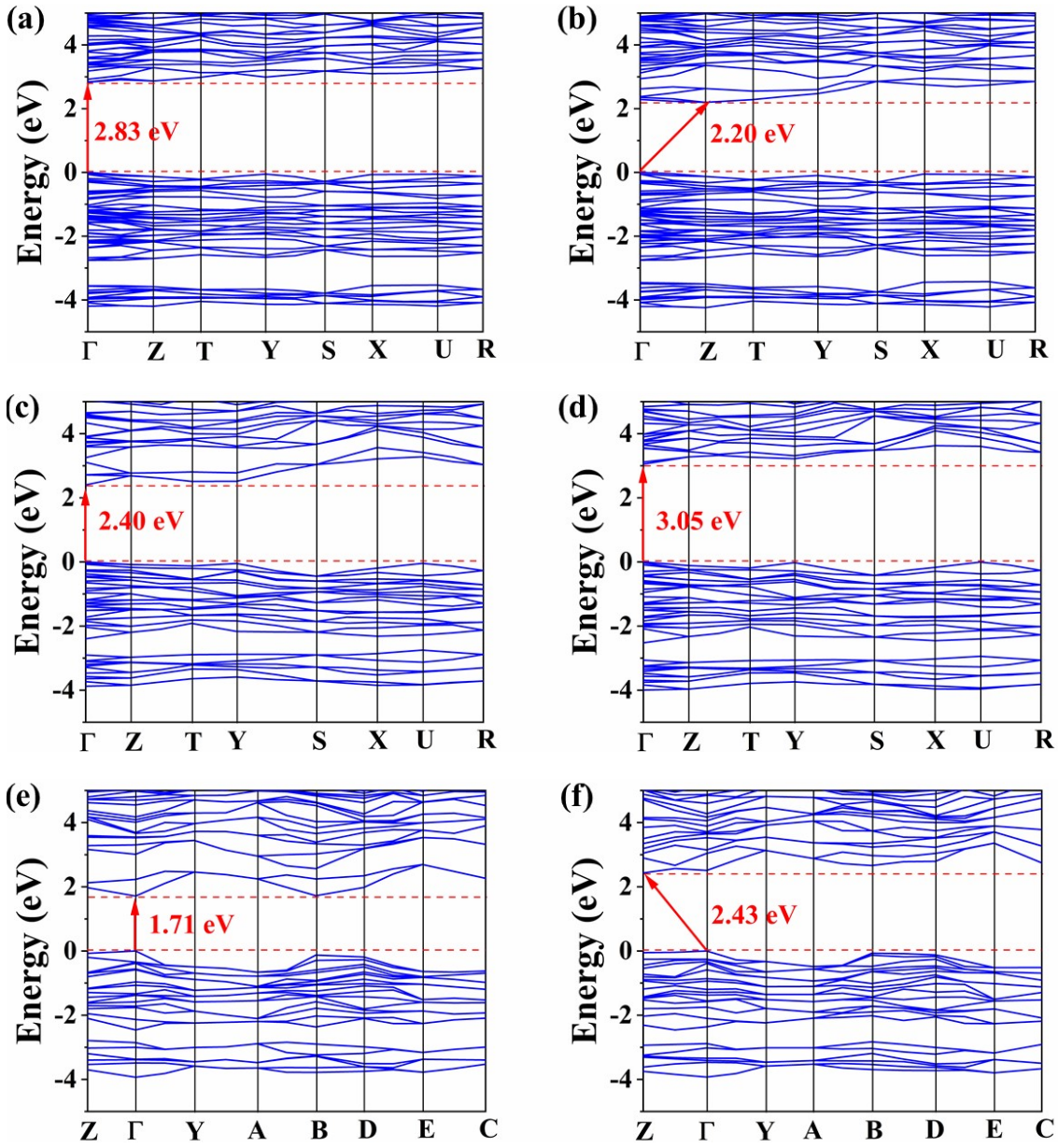

Fig. S5 Calculated band gaps of Ba_3SiS_5 (a), Ba_3GeS_5 (b), Ba_2GeS_4 (c), Ba_2SiS_4 (d), Ba_2GeSe_4 (e) and Ba_2SiSe_4 (f).

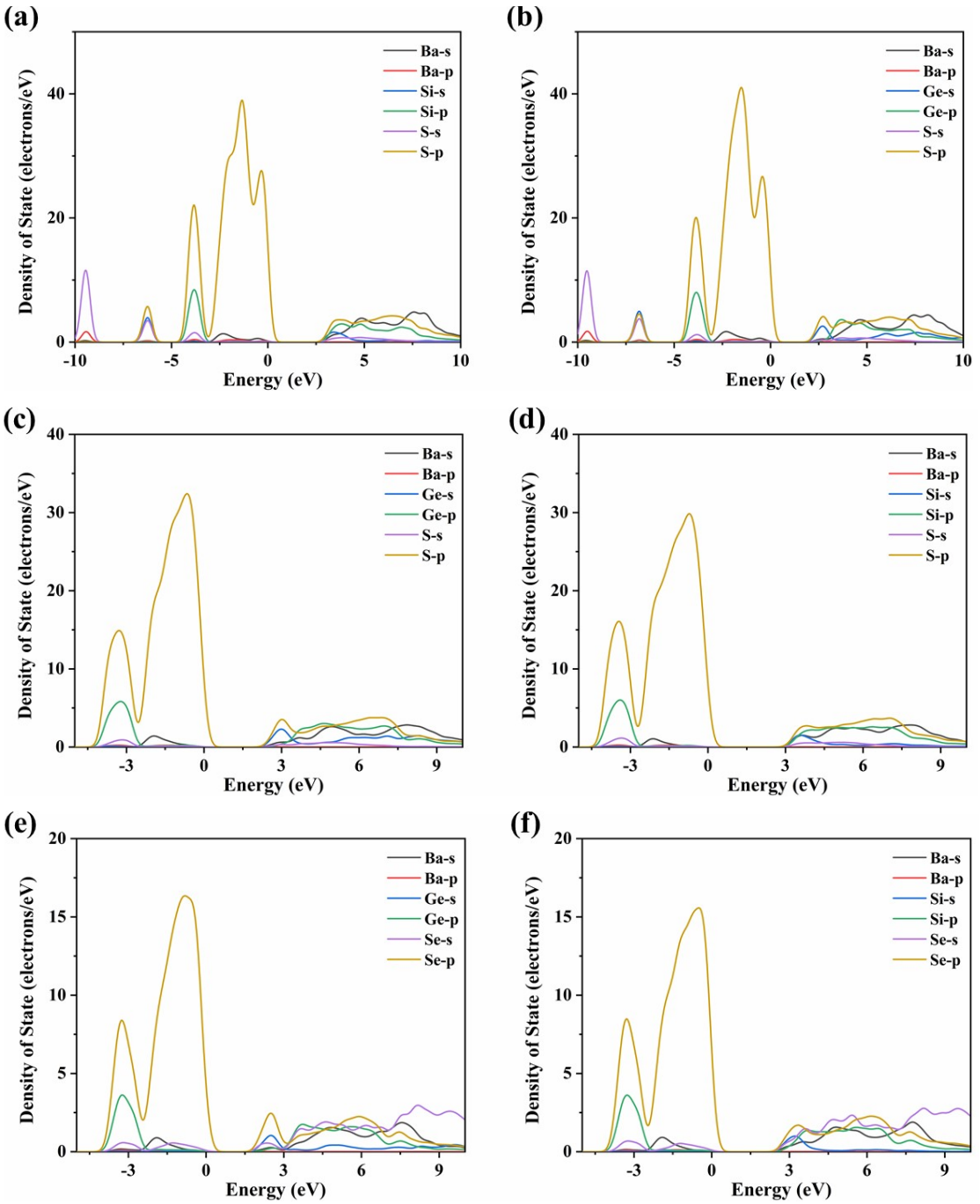

Fig. S6 The partial density of states (PDOS) of Ba_3SiS_5 (a), Ba_3GeS_5 (b), Ba_2GeS_4 (c), Ba_2SiS_4 (d), Ba_2GeSe_4 (e) and Ba_2SiSe_4 (f).

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