Supplementary Information (SI) for Journal of Materials Chemistry C.

Ba_2SiSe_4: a promising candidate with visual light transparence and p-type electrical conductivity

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1. Crystal structure

The crystal structure of Ba_2SiSe_4 is monoclinic, and it belongs to the $P2_1/m$ space group. The optimized results are shown in Table S1. In Ba_2SiSe_4, every Si is bound to four Se in tetrahedral geometry, and two crystallographically distinct Ba sites are present, and the distinct Ba sites are bound to nine and eight Se atoms with the 9-coordinated and 8-coordinated geometries, respectively. There are three unequal Se sites in the structure. At the first Se site, the Se is bound to four Ba atoms and one Si atom in a 5-coordination geometry. At the second Se site, the selenium is bound to five Ba atoms and one Si atom in a 6-coordination geometry. Similarly, at the third Se site, Se is bound to four Ba atoms and one Si atom forming the 5-coordination geometry.

Table S1. The lattice parameters, calculated with the GGA, and experimental values (Å) are listed.

parameters	this work	experiment[1]	difference
a	9.32	9.18	-1.52
b	7.12	7.03	-1.28
c	7.04	6.87	-2.47

2. The tendence of p-type electrical conductivity of Ba_2SiSe_4

According to the ionization energy criterion, when the ionization energy difference is less than 0.15 eV, which is deemed as intrinsic p-type WBSs.[2] The calculation results of the ionization energies of Ba_2SiSe_4 and common WBGs are shown in Table S2.

Table S2. The effective masses of carriers m_e^* (electrons) and m_h^* (holes) with the unit m_0, relative dielectric constant ε_r, the acceptor (donor) ionization energy E_I^A (E_I^D), and the ionization energy difference ΔE (eV) are presented.

Compound	m_e^*	m_h^*	ε_r	E_I^A	E_I^D	ΔE
$AlCuS_2$[3]	1.01	2.08	6.92	0.287	0.591	0.304
CuI[3]	0.80	1.10	3.92	0.708	0.974	0.266
$AlCuO_2$	0.92	1.00	4.61	0.588	0.640	0.052
Ba_2SiSe_4	0.49	0.21	21.97	0.014	0.006	0.008

For subsequent calculations, we used the hole effective masses and ionization potential (*IP*) obtained from the HSE hybrid functional with α=0.45 (listed in Table S3). This choice is made because while PBE-GGA and HSE06 yield negligible differences in hole effective masses, they exhibit a significant impact on the calculated *IP*. Therefore, since HSE (α=0.45) successfully reproduces the band gap,[4,5] we used this functional specifically for the calculation of the ionization potential.

Table S3. The hole effective masses (m_h^*) and ionization potential (*IP*) calculated using different functionals are listed.

	m_h^*	*IP*
PBE-GGA	0.213	-3.70
HSE06	0.210	-4.20
HSE(α=0.45)	0.211	-4.81

3. Defect Analysis

The results of all defect formation energies of Ba_2SiSe_4 calculated by DFT_GGA for specific chemical potential condition (Se-rich, Ba (Si)-poor) are shown in Fig. S1. All defect-related processes are performed by using pydefect package, including the generation of defective structures.[6] In order to accurately probe the p-type electrical conductivity, the Heyd-Scuseria-Ernzerhof hybrid functional[7] with an exact exchange fraction of 0.45 is used to calculated the defects formation energies when the defect with the formation energy is below 3.0 eV (calculated with the GGA). This method can accurately calculate the electronic structures and evaluate the defects' behavior of the material.[8]

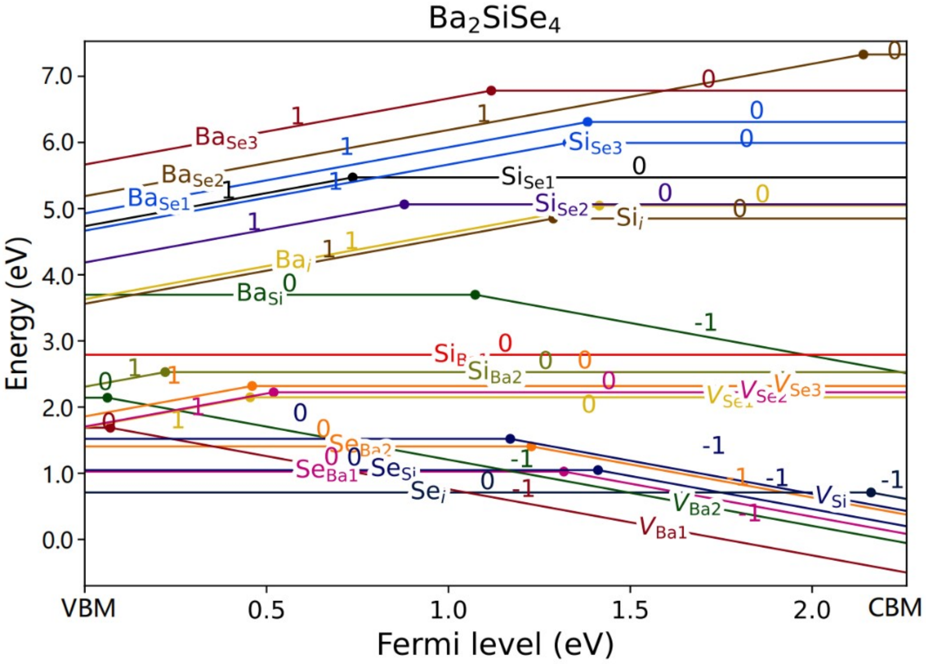

Figure S1. The formation energies of the intrinsic defects in Ba$_2$SiSe$_4$ are calculated on the basis of the GGA at a chemical potential of Se-rich, Ba (Si)-poor condition.

The defect formation energy of Ba$_2$SiSe$_4$, doped with Cs, is calculated based on the HSE (α = 0.45). And the results are presented in Fig. S2. Initial screening via GGA-PBE defect's formation energy calculations revealed that Cs substitution at the Se1 site (denoted Cs$_{Se1}$) exhibits the lowest thermodynamic stability among all possible Se-site substitutions. Consequently, HSE calculations were exclusively performed on this most stable Cs$_{Se1}$ configuration to obtain accurate electronic structure properties.

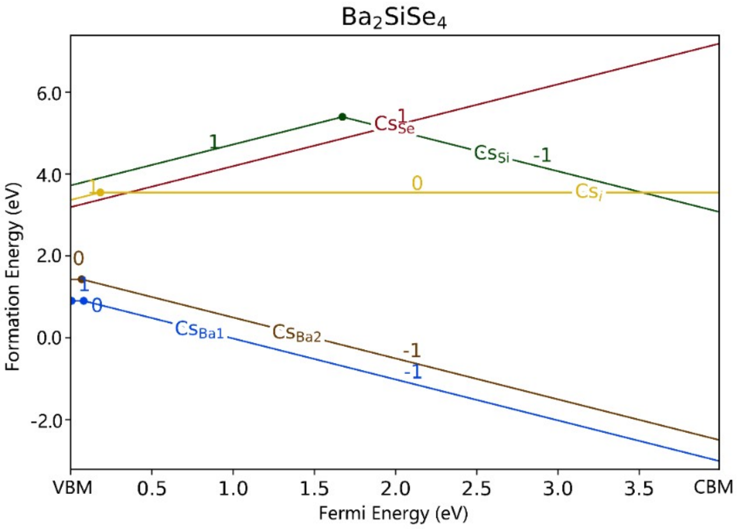

Figure S2. The defect formation energy of externally doped Cs in Ba_2SiSe_4 is calculated under Se-rich, Ba (Si)-poor condition. The chemical potential of Cs is determined from the total energy of Cs_2Se.

4. Thermodynamic simulation

With the thermodynamic equilibrium simulations, the defect densities, calculated by quenching from the preparation temperature (974.0 K) to room temperature, are presented in Table S4. At this point, the calculated hole density (n_h) in Ba_2SiSe_4 is 4.04×10^{17} cm^{-3}, and the major defects are Se_{Ba1}, Cs_{Ba1}, and Cs_{Ba1}. And the corresponding densities are $nSe_{Ba1}(0)=1.68\times10^{20} cm^{-3}$, $nCs_{Ba1}(0) = 7.60\times10^{17}$ cm^{-3}, and $nCs_{Ba1}(-)= 4.04\times10^{17}$ cm^{-3}.

Table S4. The major defects (cm^{-3}) at specified chemical potential condition (Se-rich, Ba (Si)-poor) when quenched to room temperature from the preparation temperature (974.0 K).

Type of defect	Defect density
$nSe_{Ba1}(0)$	1.68×10^{20}
$nSe_{Ba2}(0)$	1.00×10^{15}
$nCs_{Ba1}(0)$	7.60×10^{17}
$nCs_{Ba1}(-)$	4.04×10^{17}
$nCs_{Ba2}(0)$	1.06×10^{9}
$nCs_{Ba2}(-)$	9.31×10^{8}
$nSe_i(0)$	0.148
$nSi_{Ba2}(0)$	5.48×10^{2}
$nSi_{Ba2}(+)$	8.80×10^{14}

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