

# Electronic Structure and Defect Physics of Tin Sulfides: SnS, Sn<sub>2</sub>S<sub>3</sub>, and SnS<sub>2</sub>

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The tin sulfides SnS, Sn<sub>2</sub>S<sub>3</sub>, and SnS<sub>2</sub> are investigated for a wide variety of applications such as photovoltaics, thermoelectrics, two-dimensional electronic devices, Li ion battery electrodes, and photocatalysts. For these applications, native point defects play important roles, but only those of SnS have been investigated theoretically in the literature. In this study, we consider the band structures, band-edge positions, and thermodynamical stability of the tin sulfides using a density functional that accounts for van der Waals corrections and the  $GW_0$  approximation. We revisit the point-defect properties, namely, electronic and atomic structures and energetics of defects, in SnS and newly examine those in SnS<sub>2</sub> and Sn<sub>2</sub>S<sub>3</sub> with a comparison to those in SnS. We find that SnS<sub>2</sub> shows contrasting defect properties to SnS: Undoped SnS shows  $p$ -type behavior, whereas SnS<sub>2</sub> shows  $n$  type, which are mainly attributed to the tin vacancies and tin interstitials, respectively. We also find that the defect features in Sn<sub>2</sub>S<sub>3</sub> can be described as a combination of those in SnS and SnS<sub>2</sub>, intrinsically Sn<sub>2</sub>S<sub>3</sub> showing  $n$ -type behavior. However, the conversion to  $p$  type can be attained by doping with a large monovalent cation, namely, potassium. The ambipolar dopability, coupled with the earth abundance of its constituents, indicates great potential for electronic applications, including photovoltaics.

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## I. INTRODUCTION

The tin-sulfide series comprises three stable compositions, namely, SnS, Sn<sub>2</sub>S<sub>3</sub>, and SnS<sub>2</sub>. Because of their simple composition and earth-abundant and cost-effective constituent elements, a number of researchers are seeking suitable technological applications from physics, chemistry, and materials science viewpoints.

SnS has a layered structure (the distorted GeS structure) found as a mineral called herzenbergite and is stable in the presence of water and oxygen in the atmosphere. Of the tin sulfides, SnS is the most well studied and has been considered as a potential thin-film photovoltaic absorber because of its appropriate band gap of 1.1 eV and high optical-absorption coefficients ( $2 \times 10^4 \text{ cm}^{-1}$  above 1.3 eV) for past two decades [1,2]. Recently, Sinsermsuksakul *et al.* attained a photovoltaic efficiency over 4.4% [3]. However, this highest efficiency is far below the theoretical maximum efficiency of 24% [4,5]. SnS is known to represent an intrinsic  $p$ -type conductivity due to tin vacancies ( $V_{\text{Sn}}$ ) with carrier concentrations between  $10^{15}$  and  $10^{18} \text{ cm}^{-3}$  [1,3]. The band alignment at the heterojunctions between SnS and an  $n$ -type buffer layer [e.g., Zn(O,S) or CdS] and between SnS and a back-contact metal (e.g., Mo) is considered an issue of the low photovoltaic efficiency [3,6].

Therefore, the fabrication of SnS  $p$ - $n$  homojunctions might overcome the limitation of photovoltaic efficiency, but the reports on  $n$ -type conductivity are still limited and controversial [2,7,8]. SnS is also studied for thermoelectric applications thanks to its low thermal conductivity and controllable carrier density by doping [9,10]. In addition, the cleaved monolayer SnS shows potential in terms of valleytronic physics [11].

SnS<sub>2</sub> also has a layered structure, in which S ions sandwich Sn layers hexagonally, and the layers are weakly bounded by van der Waals (vdW) interactions. At a low temperature, SnS<sub>2</sub> has the simplest interlayer stacking called 2H-SnS<sub>2</sub> (the PbI<sub>2</sub> structure). SnS<sub>2</sub> is recently well studied for the Li ion battery electrode [12,13], visible-light photocatalyst for water splitting [14], gas sensor [15], and field emitter [16]. The single SnS<sub>2</sub> nanosheet is also studied as a two-dimensional semiconductor material, and recently Song *et al.* fabricated field-effect transistors and related logical gates from monolayer SnS<sub>2</sub> [17]. SnS<sub>2</sub> has a larger gap of 2.3 eV, which is suited for window layer materials in thin-film photovoltaics [18]. The carrier type of undoped SnS<sub>2</sub> is known to be  $n$  type [18–20] and, therefore, is also a potential  $n$ -type counterpart of SnS-based solar cells. The origin of the  $n$ -type behavior, however, is not yet well described.

Sn<sub>2</sub>S<sub>3</sub> has received relatively little attention in the literature so far, but herein we reveal its potential as a

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semiconductor. Specifically,  $\text{Sn}_2\text{S}_3$  is the only well-established mixed-valence tin binary compound known. For instance, the fabrication of  $\text{Sn}_3\text{O}_4$  and  $\text{SnN}$  is still challenging experimentally [21,22], whereas Steinmann *et al.* report that purchased  $\text{SnS}$  contains as much as 55% of  $\text{Sn}_2\text{S}_3$  by weight [23], indicating that  $\text{Sn}_2\text{S}_3$  is easy to make. Since the atomic framework is composed of a combination of  $\text{SnS}$  and  $\text{SnS}_2$  structures, the electronic structure is expected to be their superposition. The band gap is around 1.1 eV [18], which is close to that of  $\text{SnS}$ , but the carrier is considered  $n$  type [18], in contrast to  $\text{SnS}$ . Since lone-pair electrons commonly exist in both  $\text{SnS}$  and  $\text{Sn}_2\text{S}_3$ , the valence-band position of  $\text{Sn}_2\text{S}_3$  is expected to be close to that of  $\text{SnS}$ . Thus, the carrier type may be inverted to  $p$  type, allowing the fabrication of  $p$ - $n$  homojunctions. Given the appropriate band gap,  $\text{Sn}_2\text{S}_3$  has great potential as a solar-cell material. Indeed, the reported absorption coefficient immediately above the band gap is  $7 \times 10^3 \text{ cm}^{-1}$  [18]. On the contrary, in  $\text{SnS}$  the sizable difference between the band gap and the effective absorption threshold, which can be attributed to the indirect band gap, may cause a loss of efficiency. Furthermore, point defects in a Sn mixed-valence system have not been studied so far and are of great interest for defect physics.

In this study, we revisit the bulk properties of the tin sulfides using first-principles calculations with the generalized-gradient approximation (GGA) with a vdW correction [24–26], the Heyd-Scuseria-Ernzerhof hybrid functional (HSE06) [27–29], and the  $GW_0$  approximation [30] and discuss their electronic structures, band-edge positions, and thermodynamical stability. We also show the calculated results of native point defects using the GGA with a vdW correction along with a  $GW_0$  band-edge correction and examine the electronic properties and atomic structures of defects for each phase. For  $\text{Sn}_2\text{S}_3$ , we calculate the monovalent dopants in order to discuss the possibility of its  $p$ -type doping.

## II. COMPUTATIONAL DETAILS

All calculations are performed using the projector augmented-wave (PAW) method [31] as implemented in VASP [32,33]. PAW data sets with radial cutoffs of 1.59 Å for Sn and 1.01 Å for S are employed. Sn  $5s$  and  $5p$  and S  $3s$  and  $3p$  are described as valence electrons. For the perfect crystals, lattice constants and internal atomic positions are fully optimized until the residual stresses and forces converge to less than 0.02 GPa and 0.005 eV/Å, respectively. Wave functions are expanded by a plane-wave basis set with 550-eV cutoff energy. Calculations with the  $GW_0$  approximation [30,34,35] are conducted using a harder Sn PAW data set with a radial cutoff of 1.27 Å including  $4d$  orbitals as valence electrons.

The formation energy of a point defect is calculated as [36–38]

$$E_f[D^q] = \{E[D^q] + E_{\text{corr}}[D^q]\} - E_p - \sum n_i \mu_i + q(\epsilon_{\text{VBM}} + \Delta\epsilon_F), \quad (1)$$

where  $E[D^q]$  and  $E_p$  are the total energies of the supercell with defect  $D$  in charge state  $q$  and the perfect crystal supercell without any defect, respectively.  $n_i$  is the number of removed ( $n_i < 0$ ) or added ( $n_i > 0$ )  $i$ -type atoms, and  $\mu_i$  refers to the chemical potential. The chemical potentials can vary in the range that the host material considered is stable.  $\epsilon_{\text{VBM}}$  is the energy level of the valence-band maximum (VBM), and  $\Delta\epsilon_F$  represents the Fermi level with respect to the VBM. Apart from the approximation in the exchange-correlation functional, an error in the defect-formation energy mainly comes from the spurious electrostatic interactions between a defect cell and its images under the periodic boundary conditions, and  $E_{\text{corr}}[D^q]$  corresponds to an energy for correcting it. Here, we employ our extended Freysoldt–Neugebauer–Van de Walle (FNV) correction scheme [38,39] (see Appendix). In our scheme, we can account for the anisotropic screening of defect charges using dielectric tensors and treat systems with atomic relaxation by using the atomic-site local potential as a potential marker [38]. Note that the conventional potential alignment is unnecessary when the image-charge correction is properly applied to the defect-formation energy [38,40].

As discussed below, we perform the cell relaxation of perfect crystals with various exchange-correlation functionals: the local density approximation (LDA) [41], Perdew–Burke–Ernzerhof generalized-gradient approximation (PBE) [24], PBE with a vdW correction proposed by Grimme *et al.* with Becke–Jonson damping (PBE-D3) [25,26], and HSE06 [27–29] with (HSE06-D3) and without the vdW correction. We find that the lattice constants of the tin sulfides are best reproduced by PBE-D3 [25], and thus all defect calculations are performed with this level of theory. The band-edge positions are corrected based on the quasiparticle (QP) shifts obtained using  $GW_0$  on top of PBE ( $GW_0$ @PBE) [30]. The Green’s function is updated four times for convergence of the QP shifts.

The cutoff energy for the defect calculations is set to 280 eV, and spin polarization is considered for all defects except for those with Cu dopants, for which 300 eV is used for the calculations of supercells with and without a defect involved in Eq. (1). We emphasize that the spin polarization can reduce the energy of a defect with even-numbered electrons when a triplet is more stable than a singlet. The internal atomic positions are relaxed until the residual forces acting on all atoms are reduced to less than 0.03 eV/Å. The cell-size dependences of the defect-formation energies with and without the aforementioned size corrections are carefully checked with the defects having the largest absolute charge states in this study, which are expected to have the largest errors (see

Appendix). Finally, we adopt  $5 \times 5 \times 2$  (containing 400 atoms before introducing a defect),  $2 \times 5 \times 2$  (400 atoms), and  $6 \times 6 \times 3$  (324 atoms) supercells for SnS, Sn<sub>2</sub>S<sub>3</sub>, and SnS<sub>2</sub>, respectively, minimizing errors to less than 0.05 eV.

### III. RESULTS AND DISCUSSION

#### A. Fundamental properties of the perfect crystals

Figure 1 presents the crystal structures of  $\alpha$ -SnS (*Pnma*), Sn<sub>2</sub>S<sub>3</sub> (*Pnma*), and 2H-SnS<sub>2</sub> (*P $\bar{3}$ m1*), which are considered ground-state structures of the tin sulfides. It is noteworthy that every S ion is coordinated by three Sn in all the tin sulfides. However, the Sn—S bonds in SnS are 0.5 Å longer on average than those in SnS<sub>2</sub>, reflecting the larger ionic radius of Sn(II) with a lone pair than that of Sn(IV). Sn(II) in SnS is coordinated by three S, and the lone pair points to the interlayer free space. SnS<sub>2</sub> also has a layered structure similar to other transition-metal dichalcogenides [42], in which Sn(IV) is octahedrally coordinated by six S. The unit cell of Sn<sub>2</sub>S<sub>3</sub> is larger, contains 20 atoms, and is structurally a superposition of SnS and SnS<sub>2</sub>: Half of Sn are coordinated by three S, whereas the other half are coordinated by six S. Indeed, the Bader charges [43,44] of two Sn sites in Sn<sub>2</sub>S<sub>3</sub> are +1.0 and +1.5 when using PBE at the PBE-D3 equilibrium lattice constants, which are very close to those of SnS (+0.9) and SnS<sub>2</sub> (+1.5), respectively. The assigned Sn(II) and Sn(IV) are shown in Fig. 1(b).

Table I summarizes the calculated lattice constants of the tin sulfides using the LDA, PBE, HSE06, PBE-D3, and HSE06-D3 functionals along with experimental values. As typically found, the lattice constants are underestimated by LDA and overestimated by PBE in most cases [47]. Such tendencies are remarkable along the interlayer directions (the *c* directions for SnS and SnS<sub>2</sub> and the diagonal

directions in the *ac* plane for Sn<sub>2</sub>S<sub>3</sub>). HSE06, which usually reproduces the experimental lattice constants satisfactorily, does not improve the interlayer distances. On the other hand, PBE-D3 gives the best accordance including the interlayer distances, meaning the inclusion of the vdW interactions plays an important role for the tin sulfides. Although HSE06-D3 outperforms HSE06 overall, all the lattice constants are underestimated to some extent. Vidal *et al.* report that the interlayer distance in SnS largely correlates to defect-formation energies [1], and, thus, PBE-D3 would be suited for defect calculations of the tin sulfides.

Table II shows the theoretical band gaps obtained using LDA, PBE, and HSE06 at their equilibrium lattice constants and those using PBE, HSE06, and *GW*<sub>0</sub>@PBE at the PBE-D3 lattice constants [48]. The band-edge positions in the tin sulfides mostly lie on the lines between the special points in reciprocal space or even step out of the lines. As such, we calculate the band gaps by using a dense *k*-point sampling. Such calculations are, however, computationally too demanding when using *GW*<sub>0</sub>. Therefore, we evaluate the *GW*<sub>0</sub> band gaps from a linear interpolation of QP shifts calculated at the *k*-point grids used for typical bulk calculations. This is justified by the fact that the *k*-vector dependence of the QP shifts is rather small in the tin sulfides as also mentioned by Vidal *et al.* for SnS [49].

The LDA gaps are significantly underestimated compared to the experimental gaps, whereas the PBE gaps are in closer agreement. HSE06 usually reproduces experimental band gaps quite successfully. However, it overestimates the gaps by a few tenths of eV or more at the HSE06 equilibrium lattice constants compared to the experimental gaps. When adopting the PBE-D3 lattice constants, the gaps are reproduced by HSE06 successfully, indicating that the band gaps of the tin sulfides strongly correlate to the lattice constants. This is

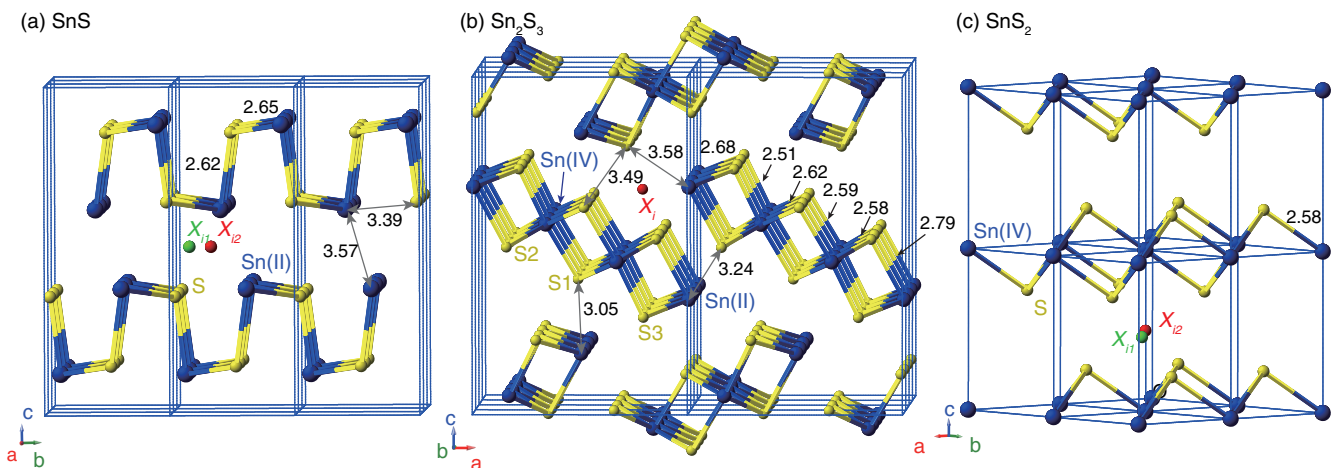


FIG. 1. Crystal structures of (a) SnS, (b) Sn<sub>2</sub>S<sub>3</sub>, and (c) SnS<sub>2</sub>. The unit cells of SnS, Sn<sub>2</sub>S<sub>3</sub>, and SnS<sub>2</sub> contain 8, 20 and 3 atoms, respectively. Large blue balls represent the Sn atoms, whereas small yellow balls represent S atoms. Sn(II) and Sn(IV) are also distinguished in Sn<sub>2</sub>S<sub>3</sub> based on the Bader charge analysis (see the text). The interstitial sites considered for the defect calculations are also depicted as  $X_{i1}$ ,  $X_{i2}$ , and  $X_i$ . The bond distances in the PBE-D3 theoretical equilibrium structures are shown in angstroms.

TABLE I. Calculated lattice constants of the tin sulfides using several exchange-correlation functionals, along with experimental values [14,45,46] (in angstroms). Mean absolute percentage errors (MAPE) compared to experimental values are also shown.

	SnS			Sn <sub>2</sub> S <sub>3</sub>			SnS <sub>2</sub>		MAPE
	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>c</i>	
LDA	3.96	4.16	10.97	8.60	3.76	13.59	3.63	5.71	2.2
PBE	4.03	4.43	11.42	9.30	3.79	14.41	3.70	6.89	3.9
HSE06	3.96	4.45	11.32	9.21	3.74	14.55	3.65	6.81	3.3
PBE-D3	4.00	4.24	11.13	8.78	3.78	13.78	3.66	5.81	1.3
HSE06-D3	3.93	4.25	10.93	8.82	3.72	13.69	3.62	5.73	1.7
Experiments	3.97	4.34	11.14	8.87	3.75	14.02	3.65	5.90	...

TABLE II. Calculated band gaps of the tin sulfides using different exchange-correlation functionals in DFT and the  $GW_0$ @PBE approximation (in eV). Structures adopted for the calculations are also shown in the second row. All the experimental values are at room temperature. Note that SnS and SnS<sub>2</sub> are known to have indirect gaps, which are relatively difficult to determine from optical-absorption measurements.

Structure	LDA	PBE	HSE06	PBE	HSE06	$GW_0$	Experiments
	LDA	PBE	HSE06	PBE-D3			
SnS	0.44	0.89	1.29	0.62	0.98	0.92	1.08 [2]
Sn <sub>2</sub> S <sub>3</sub>	0.25	0.78	1.54	0.42	0.95	1.09	1.05 [18]
SnS <sub>2</sub>	1.10	1.54	2.47	1.28	2.11	2.31	2.25 [14]

presumably because smaller lattice constants lead to larger band dispersions in the tin sulfides, which result in smaller band gaps. Consequently, such a gap lowering also occurs with PBE, but the LDA gaps increase when adopting the PBE-D3 lattice constants.  $GW_0$ @PBE reproduces the experimental gaps accurately at the PBE-D3 lattice constants. Therefore, we discuss the defect energetics using the  $GW_0$ @PBE-D3 band-edge positions in Sec. III C. We also find that spin-orbit coupling (SOC) only slightly lowers the gaps of SnS and SnS<sub>2</sub> by 0.02 and 0.05 eV and that of Sn<sub>2</sub>S<sub>3</sub> by less than 0.01 eV when using PBE, and thus the SOC is ignored in this study.

Some researchers report much larger experimental band gaps for SnS (e.g., 1.3–1.7 [50] and 1.70 eV [51]) and Sn<sub>2</sub>S<sub>3</sub> (e.g., 2 [52] and 1.9–2.2 eV [53]). These values seem unphysical, since the Sn lone-pair electrons are expected to reduce the band gaps of SnS and Sn<sub>2</sub>S<sub>3</sub> from that of SnS<sub>2</sub> as can be inferred from the tin oxides (3.6 eV for SnO<sub>2</sub> [54] and 0.7 eV for SnO [55]). Contamination of SnS<sub>2</sub> [50] or alloying with oxygen might be a part of the reason. Thus, a cautious analysis of the chemical composition is required, especially for the less-studied Sn<sub>2</sub>S<sub>3</sub>.

The band structures and density of states of the tin sulfides obtained using HSE06 at the PBE-D3 theoretical lattice constants are shown in Fig. 2. As seen, the band-edge positions deviate from the special points in the reciprocal space, except for the conduction-band minimum (CBM) of Sn<sub>2</sub>S<sub>3</sub>. The band-edge positions are, however, not conclusive in our calculations, since more than one

extremum is very close in energy at each band edge. The lone pairs of Sn-5*sp* comprise the VBM, with a bandwidth of about 2.5 eV for SnS and 1.5 eV for Sn<sub>2</sub>S<sub>3</sub>, whereas S-3*p* orbitals mainly construct that of SnS<sub>2</sub>. On the other hand, the unoccupied Sn-5*s* bands locate at the CBM of Sn<sub>2</sub>S<sub>3</sub> and SnS<sub>2</sub> with a bandwidth of about 1.5 eV for Sn<sub>2</sub>S<sub>3</sub> and 2 eV for SnS<sub>2</sub>, whereas Sn-5*p* orbitals mainly constitute that of SnS.

Slab calculations give us the band-edge positions with respect to the vacuum level and, thus, the relative positions between different solids. Figure 3(a) shows the calculated band-edge positions of the tin sulfides using PBE and  $GW_0$ @PBE at the PBE-D3 equilibrium lattice constants with and without atomic relaxations. The sign-reversed VBM positions with atomic relaxations correspond to the ionization potentials (IPs). Our calculated IP of the SnS at the (010) surface using  $GW_0$ @PBE (5.1 eV) is close to the value of 5.3 eV reported by Stevanović *et al.* using the same approximation [56].

The  $GW$  calculations change the VBM calculated by PBE rather than the CBM. We note that a similar tendency is also reported recently for various other compounds including sulfides [57–60]. The surface dipole depends on the surface orientation, and so does the band-edge position. Stevanović *et al.* show that the IP of SnS can change by up to 0.9 eV depending on the surface orientation [56]. Such a variation is remarkably large especially when comparing between Tasker type-1 and type-2 surfaces [61]. For example, the calculated IPs of



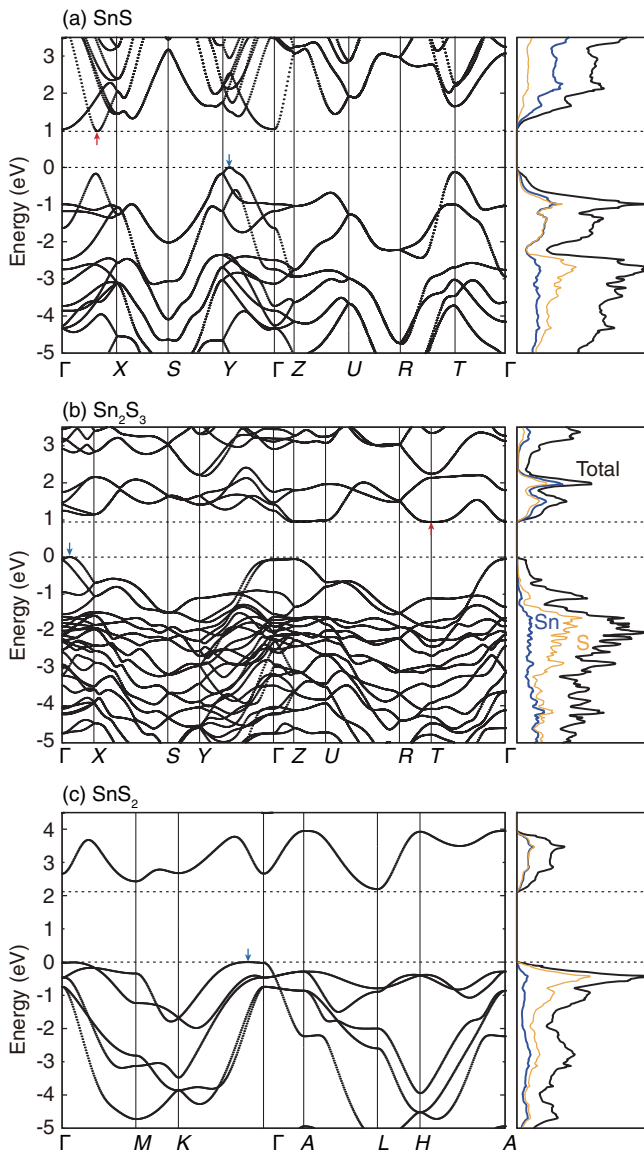


FIG. 2. Calculated band structures and density of states of (a) SnS, (b) Sn<sub>2</sub>S<sub>3</sub>, and (c) SnS<sub>2</sub> using HSE06 at the PBE-D3 equilibrium lattice constants. The energy zeros are set at the VBM. Horizontal dashed lines mean the VBM and CBM, and arrows indicate their positions in reciprocal space. Note that the CBM in SnS<sub>2</sub> does not appear in the band path shown.

rutile TiO<sub>2</sub> are 5.6 and 7.8 eV for (001) and (100) surfaces, which are categorized into Tasker type 1 and type 2, respectively [58]. As illustrated in Fig. 3(b), when anions exist on a surface exterior (Tasker type-2 surface), the potential for electrons is decreased inside a solid, which can explain why the band edges at the (001) surface in SnS<sub>2</sub> are lower than those at the (110) surface. Besides, when relaxing the (110) surface of SnS<sub>2</sub>, the sulfurs move towards the surface, as shown in Fig. 3(c), and hence the band-edge positions drop after the relaxation. Thus, to avoid such surface-derived variations, band-edge positions calculated by Tasker type-1 surfaces without atomic

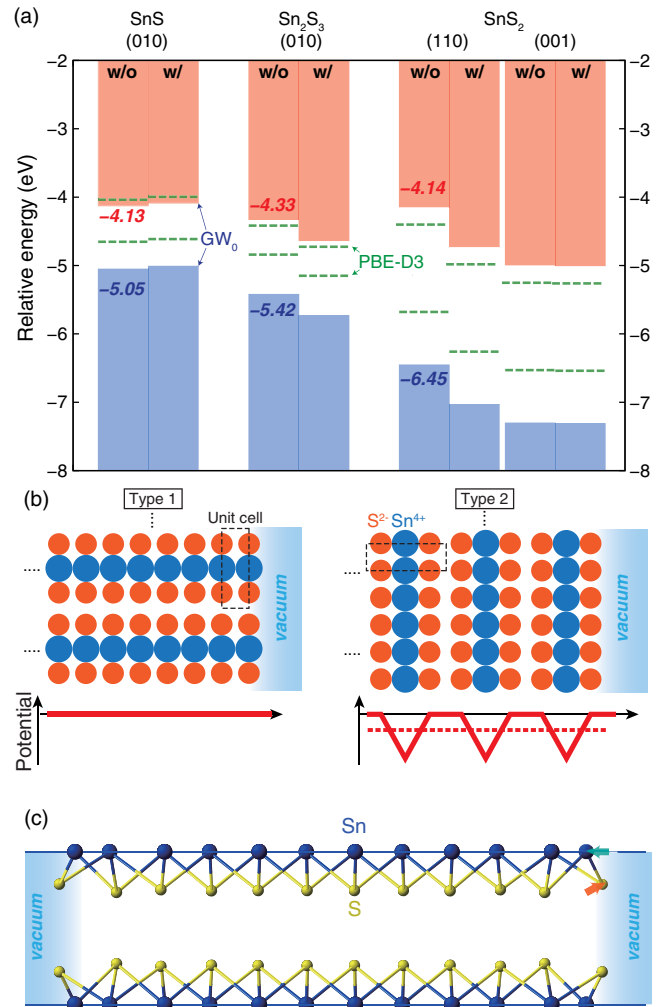


FIG. 3. (a) Band-edge positions of the tin sulfides with respect to the vacuum level calculated using PBE and  $GW_0$ @PBE at the PBE-D3 lattice constants. Both results with (w/) and without (w/o) atomic relaxation are shown. Note that the band-edge positions depend on the surface orientation. The (010) surfaces of SnS and Sn<sub>2</sub>S<sub>3</sub> and (110) surface of SnS<sub>2</sub> are classified to Tasker type 1, whereas the (001) surface of SnS<sub>2</sub> is type 2 (see the text for details). (b) Schematic illustrations of the potential shift in SnS<sub>2</sub> for electrons induced by Tasker type-1 and type-2 surfaces. Point-charge models composed of hypothetical Sn<sup>4+</sup> and S<sup>2-</sup> ions are supposed for simplicity. The unit-cell-averaged potential is shown by a dashed line. (c) Relaxed (110) surface of SnS<sub>2</sub> using a slab model with a mirror symmetry. Tins move inward, whereas sulfurs move outward near the surface, which decreases the potential for electrons inside SnS<sub>2</sub>.

relaxation are adopted for discussing the relative band-edge positions in this study.

The VBM of SnS<sub>2</sub> is 1.4 and 1.0 eV lower than those of SnS and Sn<sub>2</sub>S<sub>3</sub>, respectively. This tendency is probably due to the absence of the lone pairs in SnS<sub>2</sub> as shown above. On the other hand, the CBMs almost align in the tin sulfides. The VBM and CBM of Sn<sub>2</sub>S<sub>3</sub> are slightly lower than those of SnS. The heterojunctions between *p*-SnS and *n*-Sn<sub>2</sub>S<sub>3</sub>

could be suitable for photovoltaics, since atomic diffusion and secondary phases at the interface would not pose serious problems due to the common constituents, and the band discontinuity, which is likely to make electric loss, would be fairly low. The only remaining potential issue is the lattice mismatch.

## B. Formation energies

Figure 4 shows the convex hull of the Sn-S system at 0 K calculated using PBE, HSE06, PBE-D3, and PBE with empirical fitted element reference energies (PBE + FERE) [63], in which the energies of elements in their standard state phases are corrected so as to reproduce the experimental enthalpies of a wide variety of insulators and semiconductors. The energies of stable  $\alpha$ -Sn ( $Fd\bar{3}m$ ), SnS, Sn<sub>2</sub>S<sub>3</sub>, SnS<sub>2</sub>, and  $\alpha$ -S ( $Fddd$ ) at 0 K are considered. The accuracy of the formation energies of host materials is important for defect calculations, since they directly relate to the defect-formation energies via atomic chemical potentials. PBE and HSE06 give lower formation energies compared to the experimental values, whereas PBE-D3 and PBE + FERE show good agreement. This tendency agrees with a previous report [64]. Therefore, PBE-D3 is also suited for defect calculations from this viewpoint.

The chemical potentials of Sn and S used for evaluating point-defect-formation energies are represented as  $A$ ,  $B$ , and  $C$  in Fig. 4. Those in SnS can be varied in between  $A$  and  $B$ , whereas those in SnS<sub>2</sub> can be varied in between  $B$  and  $C$ . The energy of Sn<sub>2</sub>S<sub>3</sub> lies almost on the line

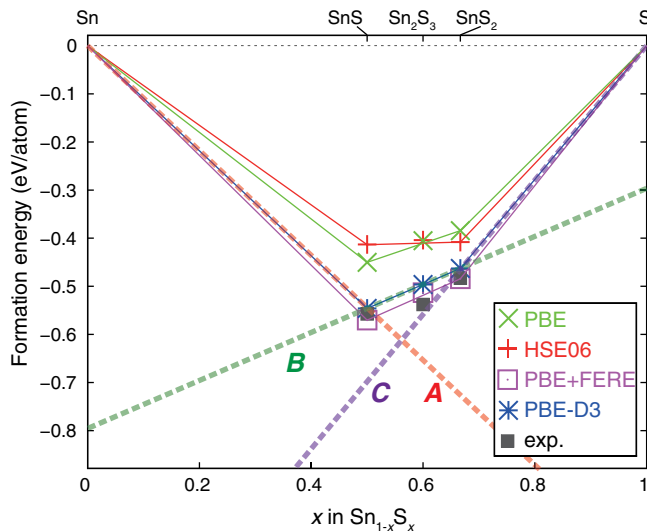


FIG. 4. The calculated formation energies of SnS, Sn<sub>2</sub>S<sub>3</sub>, and SnS<sub>2</sub> using PBE, HSE06, and PBE-D3 functionals and PBE with FERE corrections as well as those from the experiments at 298 K [62]. Three chemical potential conditions used for point-defect calculations, namely, (A) the Sn-rich condition for SnS, (B) the condition where the formation energies of SnS, Sn<sub>2</sub>S<sub>3</sub>, and SnS<sub>2</sub> lie on the tie line within less than 0.15 meV/atom, and (C) the S-rich condition for SnS<sub>2</sub>, are shown.

connecting the formation energies of SnS and SnS<sub>2</sub> denoted as  $B$ , reflecting the structural characteristics of their superposition. This means that the chemical potentials cannot be varied significantly in Sn<sub>2</sub>S<sub>3</sub> by changing the growth condition. The stability of Sn<sub>2</sub>S<sub>3</sub> could be, however, enhanced by temperature effects including phonon contributions to free energy.

## C. Point defects

Here, we discuss the formation energies and thermodynamical transition levels of native point defects and atomic defect structures in the tin sulfides. In this study, we consider vacancies, antisites, and interstitials shown in Fig. 1 and cover a wide range of charge states for each defect. Only the result with the lowest energy is shown for each defect. We also discuss the ambipolar dopability of Sn<sub>2</sub>S<sub>3</sub>, which has great potential for photovoltaics and electronic devices. It should be emphasized that the defect-formation energies can generally include errors of a few tenths of eV even after the aforementioned cell-size corrections, which come mainly from the approximation to the treatment of the electron exchange-correlation interactions.

### 1. SnS

First, we revisit native point defects in SnS using PBE-D3. Vidal *et al.* calculate the point defects using PBE and correct the PBE band-edge positions using the  $GW_0$ @PBE approximation for evaluating defect-formation energies [1]. They adopt the experimental lattice constants, since the interlayer distance is found to considerably correlate to defect-formation energies. Malone, Gali, and Kaxiras calculate impurities as well as the native point defects using PBE [65]. They adopt the PBE theoretical lattice constants and extend the CBM by 0.35 eV so as to recover the experimental gap from the underestimated PBE gap. For correcting cell-size errors on defect energetics, Vidal *et al.* adopt the scheme proposed by Lany and Zunger along with the isotropic dielectric constant [49], whereas Malone, Gali, and Kaxiras use point-charge corrections in conjunction with an anisotropic dielectric tensor [66]. Since the former and the latter are devoid of a consideration of the anisotropy of the dielectric response [67] and the influence of a finite distribution of a defect charge density, respectively, our extended FNV scheme is superior to both these schemes. Their equivalent conclusions are (i) the fabrication of  $n$ -type SnS seems difficult without doping, and (ii) tin vacancies ( $V_{\text{Sn}}$ ) are major acceptors, whereas sulfur vacancies ( $V_{\text{S}}$ ) are major donors but have a deep donor level.

Figure 5 shows the energetics of native point defects in SnS at Sn-rich (S-poor) and Sn-poor (S-rich) chemical potential conditions. Our results are close to those of Malone, Gali, and Kaxiras rather than those of Vidal *et al.*, yet the band edges are deeper in energy so that  $n$ -type

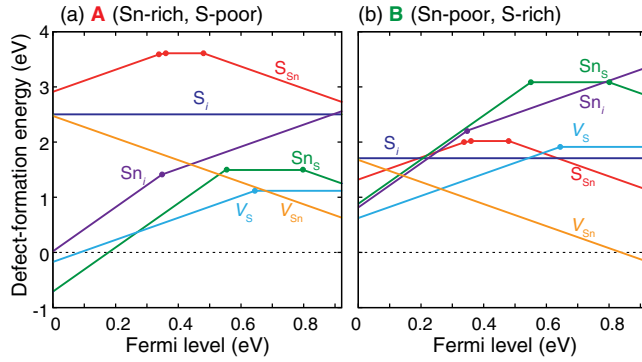


FIG. 5. Formation energies of native point defects in SnS as a function of the Fermi level under (a) Sn-rich (S-poor) and (b) Sn-poor (S-rich) chemical potential conditions. The Fermi level ranges from the valence-band maximum, which is set to zero, to the conduction-band minimum.  $V$  in defect species denote vacancies, and the subscripts denote defect sites, where  $i$  means interstitial sites. The charge states of defects correspond to the gradients. Only the most energetically favorable charge state at a given Fermi level is shown for each defect. Positive and negative charge states mean donor and acceptor behavior, respectively. The Fermi level at which the favorable charge state changes corresponds to the positions of donor or acceptor levels, which are designated by solid circles.

conversion is more plausible. This is because in our study the VBM is lowered by 0.52 eV and the CBM by 0.09 eV based on the  $GW_0$ @PBE calculation, which is in stark contrast with the upward shift of the CBM performed by Malone, Gali, and Kaxiras.

The major defects are  $V_{Sn}$  and  $V_S$ , whereas the tin and sulfur interstitials ( $Sn_i$  and  $S_i$ ) have higher energies. Although the sulfur-on-tin antisites ( $S_{Sn}$ ) have also higher energy in any condition, tin-on-sulfur antisites ( $Sn_S$ ) can be major defects at Sn-rich conditions with a lower Fermi level. At the Sn-poor condition [Fig. 5(b)], SnS takes the  $p$  type, whereas at the Sn-rich condition [Fig. 5(a)], the  $n$  type

might be attained.  $V_S$ , however, has a deep donor level, and hence it would be difficult to introduce a number of electron carriers without doping. This result is consistent with the experimental findings that undoped SnS shows  $p$ -type conductivity or high resistivity.

In experiments,  $p$ -type doping can be attained by Cu or Ag. For  $n$ -type conversion, on the other hand, aliovalent ion doping by Bi or Sb to a Sn site has not been successful to date. Ran *et al.* report that alloying Sn with Pb increases the interlayer spacing and lowers the energy of  $Sn_i$ , leading to  $n$ -type conversion at  $x > 0.15$  in  $Sn_{1-x}Pb_xS$  [2]. As can be inferred from the calculations of Malone, Gali, and Kaxiras [65] combined with our  $GW_0$  band-edge shifts, Cl doping at the Sn-rich condition might be an alternative candidate for  $n$ -type doping. Indeed, very recently, Yanagi *et al.* reported  $n$ -type SnS by Cl doping [68].

Figures 6(a)–6(d) shows the local structures near selected defects with lower formation energies in SnS.  $V_{Sn}^{-2}$  repels the neighboring S, simply because of ionic repulsion. In the case of  $V_S^0$ , neighboring Sn move inward with constructing a Sn-Sn deep localized state within the band gap. On the contrary, Sn near  $V_S^{+2}$  move outward, and the localized state locates over the CBM. This is typically found in anion vacancies including oxygen vacancy in ZnO [69]. We again perform the geometry optimization after adding two electrons ( $e^-$ ) into  $V_S^{+2}$  and see if the perturbed host states remain, but  $V_S^{+2} + 2e^-$  eventually recovers to  $V_S^0$  with a deep localized state as shown in Fig. 6(b). Intriguingly, in the case of  $Sn_S^{+4}$ , Sn displaces to the interstitial site from  $V_S$  as shown in Fig. 6(d). Therefore,  $Sn_S^{+4}$  can be regarded as a pair of  $V_S$  and  $Sn_i$ . Since  $E_f(V_S^{+2}) + E_f(Sn_i^{+2})$  is 0.59 eV lower than  $E_f(V_S^0) + E_f(Sn_i^{+4})$ ,  $Sn_S^{+4}$  should be a pair of  $V_S^{+2}$  and  $Sn_i^{+2}$ . The binding energy, namely,  $E_f(V_S^{+2}) + E_f(Sn_i^{+2}) - E_f(Sn_S^{+4})$ , is 0.88 eV. Such a split of an antisite defect into a vacancy and an interstitial is often

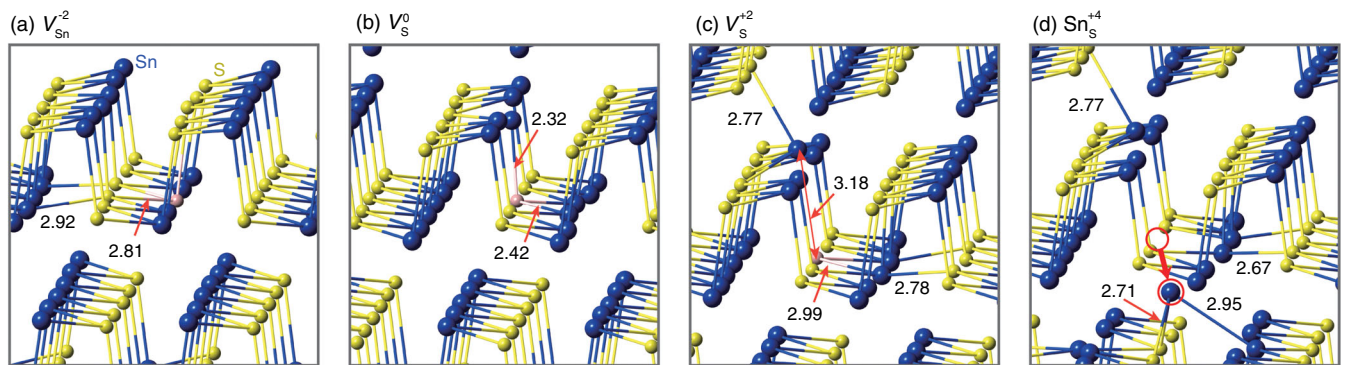


FIG. 6. Local structures of (a)  $V_{Sn}^{-2}$ , (b)  $V_S^0$ , (c)  $V_S^{+2}$ , and (d)  $Sn_S^{+4}$  in SnS. Distances between an idealized vacancy position, which is assumed to be at the original position (pink balls), and neighboring defects are shown in angstroms. As a result of the large displacement of Sn at the S site, which is highlighted by red circles and a thick arrow,  $Sn_S^{+4}$  can be regarded as a pair of  $V_S^{+2}$  and  $Sn_i^{+2}$  (see the text for details).



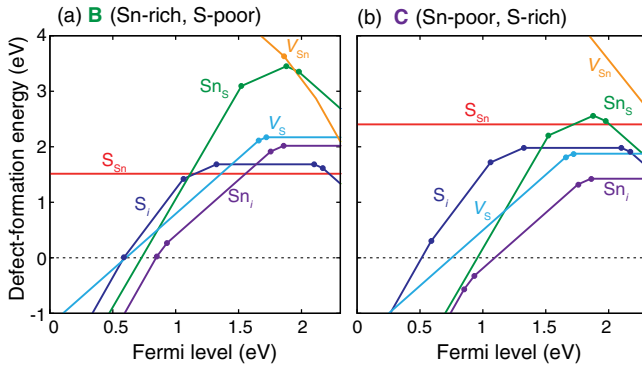


FIG. 7. Formation energies of native point defects in  $\text{SnS}_2$  as a function of the Fermi level under (a) Sn-rich (S-poor) and (b) Sn-poor (S-rich) chemical potential conditions.

found in ionic compounds. However, it seems unusual that the positively charged defects have exothermic binding energy. This would be because of the size effect:  $\text{SnS}$  does have a small interlayer space, and, in consequence,  $\text{Sn}_i$  is likely to locate near a S vacancy. Indeed,  $\text{Sn}_i^{+2}$  involves significant local structural modification with a high formation energy.

## 2. $\text{SnS}_2$

Now, we discuss the point defects in  $\text{SnS}_2$ . Although  $\text{SnS}_2$  has been intensively studied recent years, the calculations of defect properties have not been reported thus far. As in Fig. 7, our calculations predict  $n$ -type behavior of  $\text{SnS}_2$  at entire growth conditions, which is consistent with the experimental report of  $n$  type [18–20]. All the defects except for  $V_{\text{Sn}}$  can be abundant depending on the growth condition and the Fermi level. It is worth noting that the defect-formation energies in  $\text{SnS}_2$  form a contrast to those in  $\text{SnS}$  even at the same chemical potential condition  $B$ . For instance,  $V_{\text{Sn}}$  in  $\text{SnS}_2$  has much higher energy than in  $\text{SnS}$ , presumably due to a variation in the coordination numbers of Sn (six in  $\text{SnS}_2$  vs three in  $\text{SnS}$ ). On the contrary, the interstitials have much lower energies, which can be attributed to a larger free space in between weakly bounded

$\text{SnS}_2$  layers. In fact, the energies of the interstitials are lowered even in  $\text{SnS}$  when expanding the interlayer spacing by, e.g., isovalent doping with Pb [2,7]. The results shown in Fig. 7 indicate that the donor-type defects have negative formation energies when the Fermi level is lowered. In such a case, they emerge spontaneously with releasing carrier electrons, and, as a result, the Fermi level is forced up to a point at which the energies of all the donor states become zero. Since the position of such a Fermi-level pinning is so high from the VBM,  $p$ -type conversion of  $\text{SnS}_2$  cannot be attained even by external  $p$ -type doping.

Figures 8(a)–8(d) show the local structures of selected defects in  $\text{SnS}_2$ . Although  $V_{\text{S}}^0$  is not accompanied by large structural modification, the neighboring Sn construct a deep in-gap state, resulting in a deep donor level.  $\text{Sn}_i^0$  locates at the middle of the free interlayer space, with symmetric coordination distances, whereas  $S_i^0$  locates near a S with constructing a covalent bond. The distance between  $S_i^0$  and a neighboring S is 2.00 Å, which is close to those in sulfur simple substances (e.g., 2.04 Å in  $\alpha$ -sulfur). Note that such a S–S covalent bond also occurs in  $\text{SnS}$  but with a higher energy. In  $\text{SnS}_2$ ,  $\text{Sn}_i^{+4}$  is again regarded as a pair of  $V_{\text{S}}$  and  $\text{Sn}_i$ . Since  $E_f(V_{\text{S}}^{+2}) + E_f(\text{Sn}_i^{+2})$  is 1.60 eV lower than  $E_f(V_{\text{S}}^0) + E_f(\text{Sn}_i^{+4})$ ,  $\text{Sn}_i^{+4}$  should be a pair of  $V_{\text{S}}^{+2} + \text{Sn}_i^{+2}$ . The binding energy is, however, only 0.03 eV, probably because the energy gain for reducing the local strain near  $\text{Sn}_i$  is not as large as in  $\text{SnS}$  due to the larger interlayer free space in  $\text{SnS}_2$ . On the other hand,  $\text{Sn}_i^{+2}$  rests on the original Sn site with a symmetric atomic configuration with slightly shorter distances to neighboring S (2.58 → 2.46 Å).

## 3. $\text{Sn}_2\text{S}_3$

Here, we discuss the point defects in  $\text{Sn}_2\text{S}_3$ . The notations in Fig. 1(b) are used to represent irreducible atomic positions in  $\text{Sn}_2\text{S}_3$ , namely, Sn(II), Sn(IV), S1, S2, and S3. Figure 9 shows the calculated defect-formation energies. Since the point where  $E_f(\text{Sn}_i^{+2})$  and  $E_f(V_{\text{Sn(II)}}^{-2})$  intersect is close to the CBM rather than the VBM,

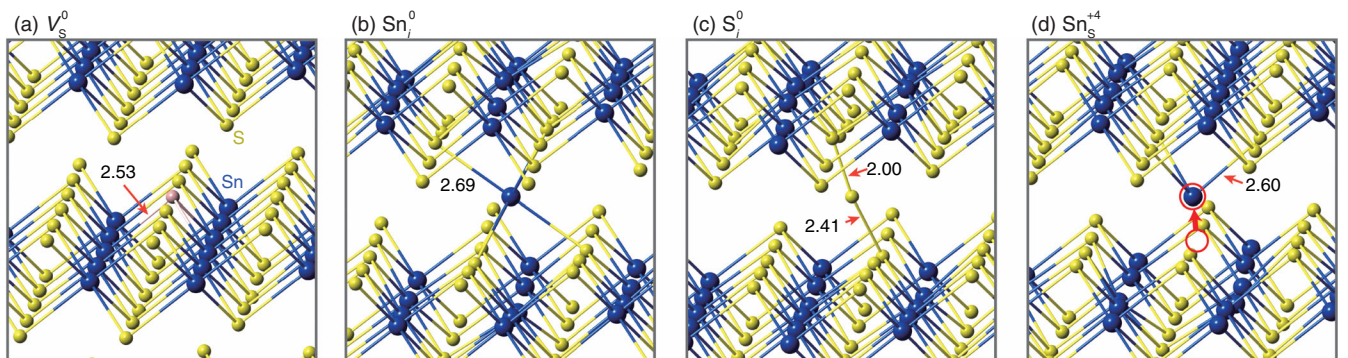


FIG. 8. Local structures of  $V_{\text{S}}^0$ ,  $\text{Sn}_i^0$ ,  $S_i^0$ , and  $\text{Sn}_i^{+4}$  in  $\text{SnS}_2$ . We note that  $\text{Sn}_i^{+4}$  can be regarded as a pair of  $V_{\text{S}}^{+2}$  and  $\text{Sn}_i^{+2}$  (see the text for details).



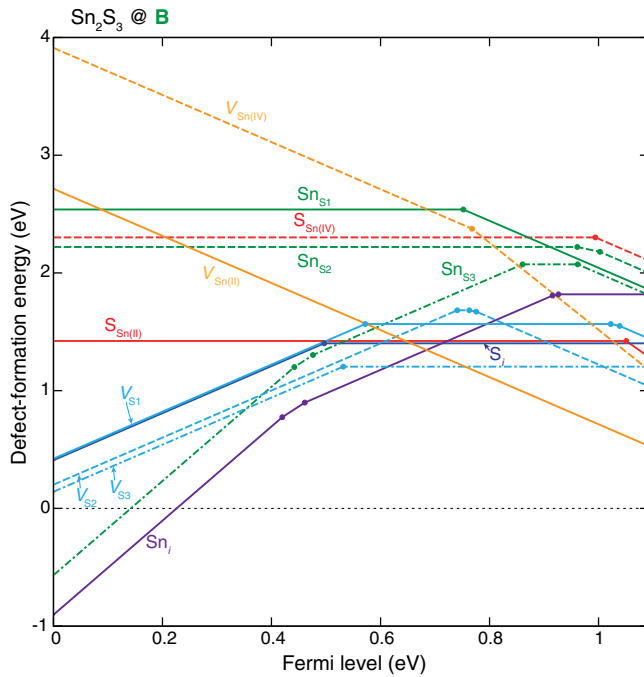


FIG. 9. Formation energies of native point defects in  $\text{Sn}_2\text{S}_3$  as a function of the Fermi level at the chemical potential condition  $B$  in Fig. 4.

undoped  $\text{Sn}_2\text{S}_3$  is expected to be  $n$  type, which is consistent with the experimental reports [18]. The other major defects are  $V_{\text{S}3}$ ,  $S_i$ , and  $S_{\text{Sn(II)}}$ , but they are mainly in neutral charge states above the middle of the Fermi level and, thus, are inert with respect to carrier generation. As represented by the higher energy of  $V_{\text{Sn(IV)}}$ , the tendency of the defect-formation energies in  $\text{Sn}_2\text{S}_3$  is generally understood from a combination of those in  $\text{SnS}$  and  $\text{SnS}_2$ . However, the formation energies of the tin vacancy and tin interstitial, which are the most stable acceptor and donor in  $\text{Sn}_2\text{S}_3$ , respectively, are not as low as those in  $\text{SnS}$  and  $\text{SnS}_2$ , respectively. These behaviors can be attributed to the differences in the band-edge positions and the size of interstitial sites. Therefore, they do not make deep Fermi-level pinning in  $\text{Sn}_2\text{S}_3$  as shown in Fig. 9.

Figures 10(a)–10(d) show the local structures of  $V_{\text{S}2}^0$ ,  $V_{\text{S}3}^0$ ,  $\text{Sn}_i^{+2}$ , and  $S_i^0$  in  $\text{Sn}_2\text{S}_3$ , respectively. Interestingly, the defect-formation energies and thermodynamical transition levels of  $V_{\text{S}1}$ ,  $V_{\text{S}2}$ , and  $V_{\text{S}3}$  are different from each other as shown in Fig. 9, even though their coordination numbers are the same. In the case of  $V_{\text{S}2}^0$ , two Sn(IV) slightly move to the vacancy site, whereas a Sn(II) repels and constructs a chemical bond with another S with keeping the same coordination number. On the contrary, in the case of  $V_{\text{S}3}^0$ , two Sn(II) repel and make new bonds with the other S each. However, one Sn(IV) comes close to the vacancy site and has lone-pair electrons pointing to the vacancy site. Therefore,  $V_{\text{S}3}^0$  can be represented as  $V_{\text{S}3}^{+2} + \text{Sn(II)}_{\text{Sn(IV)}}$ . The same situation occurs near  $V_{\text{S}1}^0$  although it is higher in energy than  $V_{\text{S}3}^0$ , because S1 is coordinated by three Sn(IV) as in  $\text{SnS}_2$ , in which  $V_{\text{S}}$  has a higher formation energy.  $\text{Sn}_i$  and  $S_i$  show almost the same tendencies as in  $\text{SnS}_2$ ;  $\text{Sn}_i$  locates in the middle of the interlayer space with a symmetric coordination environment, whereas  $S_i$  makes a covalent bond with another S.

#### 4. Overall discussion of native defects in the tin sulfides

Here, we discuss the native defects in the tin sulfides overall.

*Vacancies.*— $V_{\text{Sn(II)}}$  are lower in energy compared to  $V_{\text{Sn(IV)}}$ . Consequently,  $V_{\text{Sn(II)}}$  become a main source of native  $p$ -type conductivity in  $\text{SnS}$  and counteract carrier electrons in  $n$ -type  $\text{Sn}_2\text{S}_3$ , whereas  $V_{\text{Sn(IV)}}$  are not abundant in  $\text{Sn}_2\text{S}_3$  and  $\text{SnS}_2$  and do not significantly affect the electronic conductivity. Their energy difference can be mainly attributed to the variation in the coordination numbers [three of Sn(II) vs six of Sn(IV)], since the vacancy formation energy generally increases with increasing the coordination number. On the other hand, although  $V_{\text{S}}$  have rather low energies especially in  $\text{SnS}$  and  $\text{Sn}_2\text{S}_3$ , they have deep donor levels.

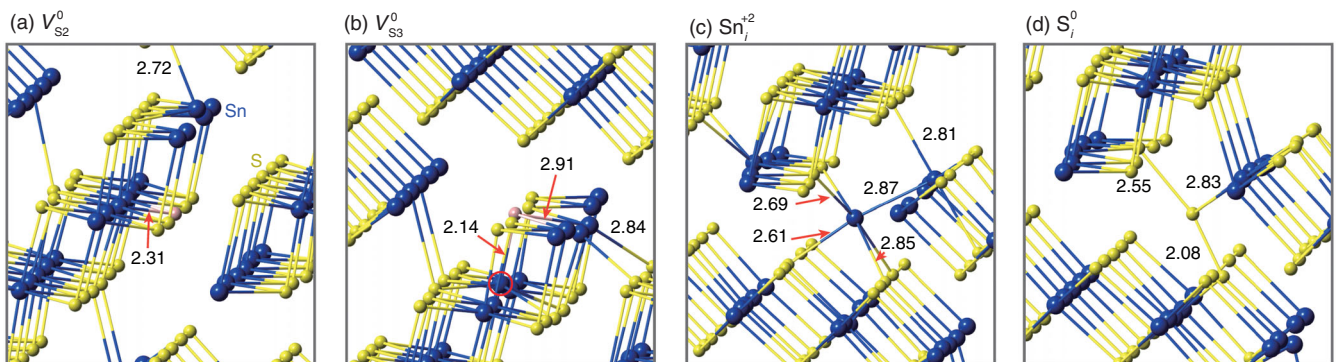


FIG. 10. Local structures of  $V_{\text{S}2}^0$ ,  $V_{\text{S}3}^0$ ,  $\text{Sn}_i^{+2}$ , and  $S_i^0$  in  $\text{Sn}_2\text{S}_3$ . The Sn changing the oxidation state from +4 to +2 near an S3 vacancy is highlighted by a red circle.

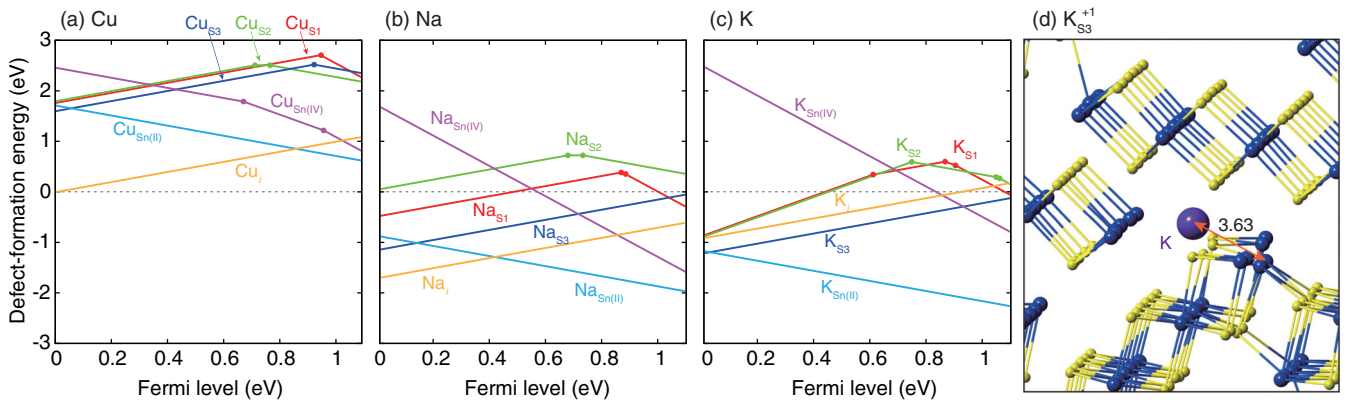


FIG. 11. Formation energies of (a) Cu, (b) Na, and (c) K dopants in  $\text{Sn}_2\text{S}_3$  as a function of the Fermi level at the chemical potential condition  $B$  in Fig. 4. The chemical potentials of the dopants are fixed to the energies of their simple substances (see the text for details). (d) A local structure of  $\text{K}_{\text{S}_3}^{+1}$  in  $\text{Sn}_2\text{S}_3$ .

*Interstitials.*—The formation energy of an interstitial strongly correlates to the size of the interlayer free space in the tin sulfides and, thus, decreases from  $\text{SnS}$  to  $\text{Sn}_2\text{S}_3$  to  $\text{SnS}_2$ .  $\text{Sn}_i$  is likely to locate at the center of the free space, whereas  $\text{S}_i$  prefers to make a covalent bonding with a neighboring S with keeping the S—S distance close to that in  $\alpha$ -sulfur.  $\text{Sn}_i$  acts as a deep donor in  $\text{Sn}_2\text{S}_3$  and  $\text{SnS}_2$  but a shallow donor in  $\text{SnS}$ . Therefore,  $n$ - $\text{SnS}$  can be attained when the energy of  $\text{Sn}_i$  is decreased by increasing the interlayer free space via, e.g., alloying with PbS [2,7]. On the contrary,  $\text{S}_i$  are amphoteric with very deep donor and acceptor levels in all the tin sulfides.

*Antisites.*—The formation energy of an antisite strongly depends on the chemical potential condition, since the chemical potentials of two species are involved in the formation energy. The antisites do not play important roles in the tin sulfides in most cases compared to vacancies and interstitials due to their higher formation energies. In all the tin sulfides,  $\text{Sn}_\text{S}$  with a lower energy largely moves from the original S site to free space nearby. Therefore,  $\text{Sn}_\text{S}$  can be regarded as a combination of  $\text{Sn}_i$  and  $V_\text{S}$ . The exothermic binding energy between  $\text{Sn}_i$  and  $V_\text{S}$  increases as the interlayer space is decreased. On the other hand,  $\text{S}_{\text{Sn}}$  is likely to locate at the original Sn site with a higher energy and very deep donor and/or acceptor levels.

### 5. $p$ -type doping in $\text{Sn}_2\text{S}_3$

As discussed in Sec. III C 3, the major carriers in undoped  $\text{Sn}_2\text{S}_3$  are electrons. In contrast to  $\text{SnS}_2$ , however,  $p$ -type conversion might be plausible with external doping, since the Fermi-level pinning caused by  $\text{Sn}_i$  occurs at just 0.23 eV above the VBM (see Fig. 9). At this Fermi level, the hole carrier density at room temperature estimated from the density of states shown in Fig. 2(b) is  $3 \times 10^{15} \text{ cm}^{-3}$ . The substitution of Sn with cations having fewer oxidation

states may introduce holes, and hence monovalent elements would be suited since their oxidation states are lower than those of both Sn(II) and Sn(IV). However, cations locating at the interstitial sites, which generally counteract holes or even introduce carrier electrons, can be easily formed in the tin sulfides. Therefore, monovalent atoms with large ionic radii would be suited for  $p$ -type doping in  $\text{Sn}_2\text{S}_3$ . Here, we test this hypothesis through calculations of Cu, Na, and K dopants in  $\text{Sn}_2\text{S}_3$ .

The calculated results are shown in Figs. 11(a)–11(c). Note that the ionic radii increase from Cu (0.74 Å for 1 + oxidation state with 4-coordination) to Na (1.13 Å) to K (1.51 Å) [70]. It may be plausible to dope more impurities than their equilibrium concentrations when quenching materials or using nonequilibrium techniques such as ion implantation. Therefore, in this study, we discuss the relative formation energies of dopants. The chemical potentials of the dopants are fixed to the energies of their simple substances, and the possibility of secondary phases composed of the dopant and Sn and/or S is excluded.

As we expect, Cu, which has the smallest ionic radius among the dopants considered, is likely to locate at the interstitial site. Since the intersection point of  $E_f(\text{Cu}_i^{+1})$  and  $E_f(\text{Cu}_{\text{Sn(II)}}^{-1})$  is near the CBM, Cu doping releases electron carriers. In the case of Na, the substitutional Na are more likely than interstitial ones when the Fermi level locates at the middle of the band gap or higher, and, as we expect, this tendency is more pronounced when doping K. As a result,  $E_f(\text{K}_{\text{S}_3}^{+1})$  and  $E_f(\text{K}_{\text{Sn(II)}}^{-1})$  intersect just above the VBM, indicating that the K doping allows us to make  $p$ - $\text{Sn}_2\text{S}_3$ .

Interestingly,  $\text{K}_{\text{S}_3}^{+1}$  has a significantly lower formation energy even compared with  $\text{K}_i^{+1}$ . As shown in Fig. 11(d) illustrating the local structure of  $\text{K}_{\text{S}_3}^{+1}$ , the K ion moves from the original S site to free space nearby as  $\text{Sn}_\text{S}$  antisites do. This is presumably because a K preferentially couples with

a S vacancy so as to reduce the local strain caused by a large K.

#### IV. CONCLUSIONS

We revisit the lattice constants, electronic structures, and band alignments of the tin sulfides using the PBE + D3 functional and  $GW_0$ @PBE approximation. It is found that consideration of vdW interactions is important for reproducing the lattice constants of the tin sulfides, especially along the interlayer directions. Based on the Bader charge analysis, half of Sn in  $\text{Sn}_2\text{S}_3$  are assigned to Sn(II) and the other half to Sn(IV), which is also consistent with their local coordination environments. Regarding the band gaps,  $GW_0$ @PBE at the PBE-D3 lattice constants shows good agreement with experimental values. The VBM position lowers from SnS to  $\text{Sn}_2\text{S}_3$  to  $\text{SnS}_2$ , whereas the CBM does not change significantly. We also calculate the convex hull of the Sn-S system and find that PBE-D3 can reproduce the experimental formation energies quite well. As a result,  $\text{Sn}_2\text{S}_3$  is found not to be very stable with respect to SnS and  $\text{SnS}_2$ . This, however, seems natural, since its structural feature is described by a superposition of those of SnS and  $\text{SnS}_2$ .

In the latter part of this paper, we systematically investigate the native point defects in the tin sulfides, i.e., vacancies, interstitials, and antisites using the PBE + D3 functional and the band-edge shift calculated by the  $GW_0$ @PBE approximation. In addition, we calculate the properties of monovalent dopants (Cu, Na, and K) in  $\text{Sn}_2\text{S}_3$  to introduce a guide for achieving  $p$ -type  $\text{Sn}_2\text{S}_3$ . The spurious electrostatic errors in the defect-formation energies caused by the supercell modeling are removed using our extended FNV scheme. The native SnS is found to be  $p$  type or  $n$  type with a low carrier concentration depending on the growth conditions. The major defects in SnS are  $V_{\text{Sn}}$  and  $V_{\text{S}}$ , which are a shallow acceptor and a deep donor, respectively.  $\text{SnS}_2$  is found to be  $n$  type primarily due to

$\text{Sn}_i$ , which have a lower formation energy than in SnS.  $\text{SnS}_2$  is difficult to be inverted to  $p$  type even by external doping because of the deep Fermi-level pinning of  $\text{Sn}_i$ . The dominant point defects in  $\text{Sn}_2\text{S}_3$  are  $V_{\text{Sn(II)}}$ ,  $\text{Sn}_i$ , and  $V_{\text{S}}$ , which are a shallow acceptor, a shallow donor, and a deep donor, respectively. The calculated undoped  $\text{Sn}_2\text{S}_3$  is  $n$  type that is consistent with the experimental findings. To make  $p$ - $\text{Sn}_2\text{S}_3$ , we propose to dope with K because of its large ionic radius, which is a necessity to prevent the incorporation of dopants into the interstitial sites.

#### ACKNOWLEDGMENTS

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#### APPENDIX: ENERGY CORRECTIONS FOR POINT DEFECTS

We here focus on errors in the defect-formation energies caused by the finite sizes of supercells and how accurately they are corrected using *a posteriori* electrostatics-based corrections. More details are discussed in Ref. [38]. In Fig. 12, the relative formation energies of  $\text{Sn}_S^{+4}$  in SnS,  $V_{\text{Sn(IV)}}^{-4}$  in  $\text{Sn}_2\text{S}_3$ , and  $V_{\text{Sn(IV)}}^{-4}$  in  $\text{SnS}_2$  are shown as functions of supercell sizes. These defects have the largest absolute charge states in this study, which are likely to have the largest error in each system. When compared with similar-size supercells, the absolute error increases from SnS to  $\text{Sn}_2\text{S}_3$  to  $\text{SnS}_2$ , because the error is roughly proportional to the reciprocal of a dielectric constant (see Table III) when the supercell size is the same. Note that the ionic contribution to the dielectric constant of  $\text{SnS}_2$

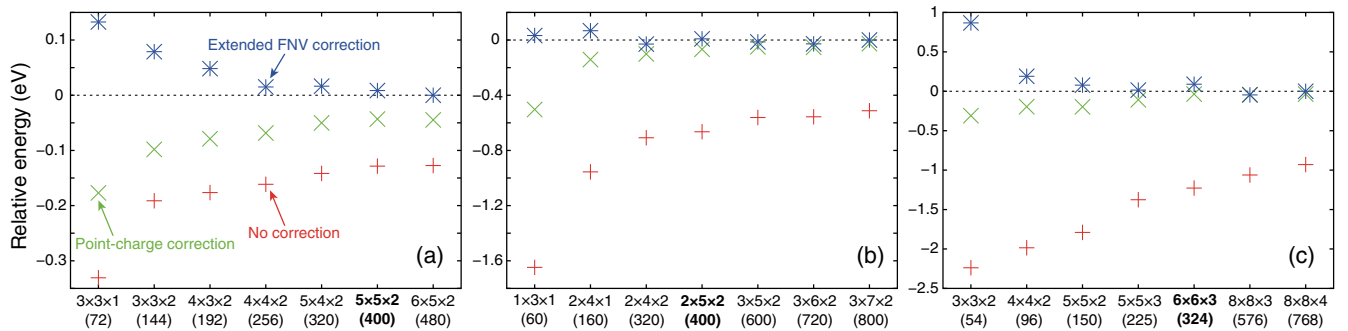


FIG. 12. Uncorrected, point-charge-corrected, and extended FNV-corrected relative defect-formation energies of (a)  $\text{Sn}_S^{+4}$  in SnS, (b)  $V_{\text{Sn(IV)}}^{-4}$  in  $\text{Sn}_2\text{S}_3$ , and (c)  $V_{\text{Sn(IV)}}^{-4}$  in  $\text{SnS}_2$  as functions of supercell sizes. Zeros of the relative energies are set to the FNV-corrected energies with the largest supercells. The values in parentheses are the numbers of atoms in the supercells before introducing a defect. Supercell sizes in boldface type are used for the defect calculations in this study. Calculations are performed using PBE-D3 at its theoretical lattice constants.



TABLE III. Calculated ion-clamped dielectric tensors ( $\epsilon^{\text{ele}}$ ) and ionic contributions ( $\epsilon^{\text{ion}}$ ) of SnS, Sn<sub>2</sub>S<sub>3</sub>, and SnS<sub>2</sub> using PBE at the PBE-D3 theoretical lattice constants.

	SnS			Sn <sub>2</sub> S <sub>3</sub>			SnS <sub>2</sub>	
	$\epsilon_{11}$	$\epsilon_{22}$	$\epsilon_{33}$	$\epsilon_{11}$	$\epsilon_{22}$	$\epsilon_{33}$	$\epsilon_{11}$	$\epsilon_{33}$
$\epsilon^{\text{ele}}$	19.8	16.8	16.5	11.5	11.4	12.1	8.5	6.7
$\epsilon^{\text{ion}}$	40.4	21.7	19.2	9.67	15.5	15.4	10.3	0.6

along the out-of-plane direction is relatively small, indicating SnS<sub>2</sub> holds more two-dimensional characteristics than the others.

We also show the relative defect-formation energies with point-charge corrections and extended FNV corrections in Fig. 12. In order to consider the anisotropic features, dielectric tensors are utilized for evaluating the point-charge potential and energies in both cases [38]. These corrections drastically improve the defect-formation energies. The FNV corrections take into account the finite defect-size effect and, hence, are usually superior to the point-charge ones. This is, however, not true when adopting smaller supercells as seen in SnS<sub>2</sub>, because the other errors not considered in the extended FNV correction scheme may cancel out the difference fortuitously. Therefore, it is better to choose supercells with small errors after applying the FNV corrections. Based on the test calculations, we adopt  $5 \times 5 \times 2$ ,  $2 \times 5 \times 2$ , and  $6 \times 6 \times 3$  supercells for SnS, Sn<sub>2</sub>S<sub>3</sub>, and SnS<sub>2</sub>, respectively, which allow us to estimate the defect-formation energies within an error of 0.05 eV.

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