

Chalcogenide perovskites: an emerging class of semiconductors for optoelectronics

Pooja Basera* and Saswata Bhattacharya*

Department of Physics, Indian Institute of Technology Delhi, New Delhi, India

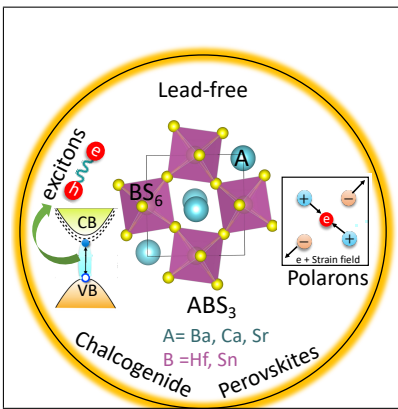
E-mail: Pooja.Basera@physics.iitd.ac.in[PB]; saswata@physics.iitd.ac.in[SB]

Phone: +91-11-2659 1359

Abstract

Chalcogenide perovskites have received considerable interest in photovoltaic research community owing to their stability (thermal and aqueous), non-toxicity and lead free composition. However, to date a theoretical study mainly focusing on the excitonic and polaronic properties are not explored rigorously, due to its huge computational demand. Herein, we capture the excitonic and polaronic effects in a series of chalcogenide perovskites ABS_3 where $A=\text{Ba, Ca, Sr}$, and $B=\text{Hf, Sn}$ by employing state-of-the-art hybrid density functional theory and many body perturbative approaches viz. GW and BSE. We find that these perovskites possess a large exciton binding energy than 3D inorganic-organic hybrid halide perovskites. We examine the interplay of electronic and ionic contribution to the dielectric screening, and conclude that electronic contribution is dominant over the ionic contribution. Further using Feynman polaron model, polaron parameters are computed, and we observe that charge separated polaronic states are less stable than bound excitons. Finally, the theoretically calculated spectroscopic limited maximum efficiency (SLME) suggests that among all chalcogenide perovskites, CaSnS_3 could serve as a best choice for photovoltaic applications.

Graphical TOC Entry



Keywords

chalcogenide perovskite, hybrid DFT, GW-BSE, excitons, polarons, exciton binding energy, SLME

Perovskites have gained unprecedented attention in the past few years owing to their versatile chemical and physical properties, and lead to a breakthrough progress from 3.8% to 25.5% .^{1,2} This indicates that device performance is intimately linked with basic material properties. The suitable material characteristics allow to significantly shorten the time period for the evolution of high-efficiency cells. However, the toxicity, degradability and the instability are still serious challenges for large scale industrial applications.^{3,4} This motivates researchers towards a new species of perovskites, namely, chalcogenide perovskites that possess Pb-free composition, are earth-abundant, and highly stable in ambient atmosphere.^{5,6} Several studies have been performed experimentally as well as theoretically that show the successful formation of chalcogenide perovskites along with their promising properties.^{7-9,9-18} Perera *et al.* have synthesised $AZrS_3$ ($A = Ba, Ca, Sr$) using high temperature sulfurization of the oxides with CS_2 .¹⁹ S. Niu *et al.* have also synthesized them as well as probed the optoelectronic properties experimentally.²⁰ Meng *et al.* predicted mixed perovskites chalcogenides $BaZr_{1-x}Ti_xS_3$ by repeated annealing of binary mixtures.²¹ Sun *et al.* proposed S and Se based perovskites and predicted their suitable band gaps for single junction solar cell.²² However, most of the earlier experimental and theoretical studies are mainly focused on Zr-based chalcogenide perovskites.²³ Recently, a few reports in the literature presented a first-principles studies for Sn based chalcogenides as a high performance thermoelectric materials,²⁴ and Hf based chalcogenides as green light emitting semiconductors.²⁵ In addition, a recent experimental studies successfully unveil the synthesis of $CaSnS_3$ perovskite.²⁶ In view of this, we aim to provide a detailed theoretical study for Hf and Sn- based chalcogenides concerning the properties suitable for optoelectronic applications that may act as valuable guidance for the ongoing experimental work.

Intriguingly, the charge separation in these materials are considerably affected by the exciton formation. The operation behind the solar cell mechanism depends on the thermally dissociate excitons into free electrons and holes, which in turn induce free-charge transport. Therefore, the accurate determination of the exciton binding energy is crucial for their active

usage in optoelectronic materials. Additionally, the charge carrier and exciton dynamics are also influenced by the polaron formation. The multiple photophysical phenomena in these materials can be explained by electron-phonon interactions and the transport of polarons.^{27,28} Regardless of several studies on chalcogenide perovskites, a thorough understanding on excitonic and polaronic effects on Hf and Sn-based chalcogenides are hitherto unknown, and unveil for the first time, to the best of our knowledge.

In this Letter, we have performed a robust study of electronic, optical, excitonic and polaronic properties of chalcogenide perovskites ABS_3 (where A= Ba, Ca, Sr, and B=Hf, Sn) within the framework of density functional theory (DFT),^{29,30} hybrid DFT (HSE06) and beyond DFT approaches (GW and BSE). First, we optimize the crystal structures using semi-local PBE³¹ exchange-correlation (ϵ_{xc}) functional, and validate the optimized lattice parameters in light of the available experimental results. Then, to study electronic structure, atom-projected electronic partial density of states (pDOS) are computed using hybrid ϵ_{xc} functional HSE06.³² Subsequently, the optical properties are determined using many-body perturbation theory (MBPT). Then, we solve the Bethe-Salpeter equation (BSE)^{33,34} on top of single-shot $G_0W_0@PBE$,^{35,36} to obtain the exciton binding energy as well as electronic contribution to the dielectric function. On the other hand, the ionic contribution to the dielectric function is determined using density functional perturbation theory (DFPT). Finally, we compute the spectroscopic limited maximum efficiency (SLME)³⁷ using the quasiparticle (QP) band gap and absorption coefficient.

Herein, we consider the distorted orthorhombic phase of chalcogenide perovskites ABS_3 (A=Ba, Ca, Sr, and B=Hf, Sn) having the space group $Pnma$ ⁷ (see Figure 2a). For $BaSnS_3$ and $SrSnS_3$, the needle-like phase is examined in our study. Table 1 presents the PBE ϵ_{xc} functional optimized lattice parameters, which are closely in agreement with experimental results reported in literature. In addition, the octahedra distortions (BS_6) for ABS_3 chalcogenides are also listed in Table1. The average bond length, bond angle variance, polyhedral volume and distortion index are calculated corresponding to BS_6 octahedra. The data shows

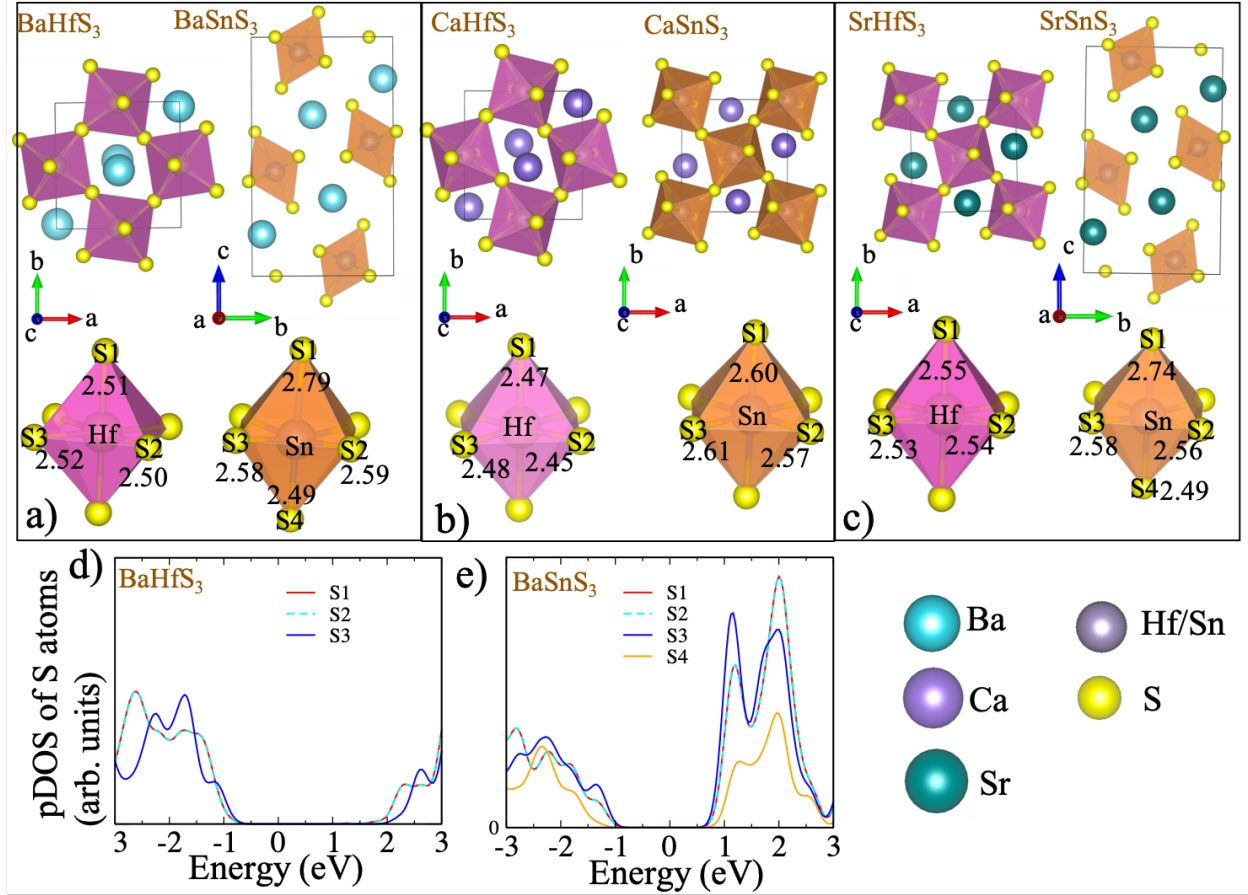


Figure 1: Crystal structure (a) BaHfS₃ in orthorhombic distorted phase and BaSnS₃ in needle-like phase. (b) CaHfS₃ and CaSnS₃ in orthorhombic distorted phase. (c) SrHfS₃ in orthorhombic distorted phase and SrSnS₃ in needle-like phase. Sulphur atom projected density of states (d) BaHfS₃ and (e) BaSnS₃

that the BS₆ octahedra in chalcogenides having needle like phase (BaSnS₃ and SrSnS₃) is more distorted compared to octahedra in orthorhombic phase (see Fig 1 and Table 1). In BaSnS₃ and SrSnS₃, there are four types of Sn-S bonds of different strengths, namely S1, S2, S3, S4 (see Fig 1[a-c]). We notice that Sn-S1 bonding is relatively weaker, however Sn-S4 bonding is the strongest one. The atom-projected density of states are calculated to disentangle the contribution of each S atoms at valence band edges (Note that S atom has main contribution at valence band maximum for these perovskites (vide infra)). For BaHfS₃, the S1, S2 and S3 contribution are same at valence band edges, because of almost same binding strength with Hf atom, however for BaSnS₃, Sn-S4 has stronger binding that leads to

Table 1: Calculated lattice parameters of ABS_3 (A=Ba, Ca, Sr and B = Hf, Sn) chalcogenide perovskites. The experimental values are provided in brackets, and are taken from Ref. ^{7,26,38} Calculated distortion parameters for BS_6 octahedra in ABS_3 chalcogenide perovskites.

Configurations	a (Å)	b (Å)	c (Å)	
BaHfS ₃	6.95 (6.99)	6.99 (7.00)	9.99 (9.92)	
BaSnS ₃	3.97 (3.93)	8.48 (8.53)	15.35 (14.51)	
CaHfS ₃	6.39 (6.52)	6.89 (6.98)	9.35 (9.54)	
CaSnS ₃	6.72 (6.68)	7.06(7.08)	9.67 (11.28)	
SrHfS ₃	6.77 (6.72)	7.09 (7.05)	9.77 (9.72)	
SrSnS ₃	3.78 (3.79)	8.41 (8.74)	14.62(14.08)	
Octahedra (BS ₆)	Average bond length (Å)	Bond angle variance (deg. ⁽²⁾)	Polyhedral volume (Å ³)	Distortion index
BaHfS ₃ (HfS ₆)	2.51	0.29	21.04	0.0036
BaSnS ₃ (SnS ₆)	2.61	19.61	23.38	0.024
CaHfS ₃ (HfS ₆)	2.47	1.14	20.06	0.00513
CaSnS ₃ (SnS ₆)	2.59	3.22	23.23	0.00513
SrHfS ₃ (HfS ₆)	2.54	0.15	21.86	0.00377
SrSnS ₃ (SnS ₆)	2.59	15.72	22.92	0.01958

its least contribution at valence band edges (see SI, Fig S3, for remaining configurations).

Therefore, the differentiation of S atoms at valence band edges subsequently lead to lighter valence bands (low m_h^*), which eventually helps to boost the hole mobility (Table 2).

To gain deep insights on the electronic structure, we compute the electronic pDOS of the ABS_6 chalcogenides using HSE06 ϵ_{xc} functional as shown in Figure 2[a-f]. For AHfS₃ perovskites, the valence band maximum (VBM) is majorly contributed by S 3p-orbitals, whereas Hf 4d-orbitals primarily contributed at the conduction band minimum (CBm). The remaining orbitals have minor contribution at VBM and CBm. For ASnS₃ perovskites, the VBM is mainly contributed by S 3p -orbitals, the CBm is dominated by the hybridization of S (3p) and Sn (5s) orbitals. The presence of hybridized states in case of ASnS₃ perovskite is responsible for its lower band gap than AHfS₃ perovskites, the latter does not contain hybridized states. The orbitals and their hybridization can be visualized clearly from wave function analysis. For BaHfS₃, the S p orbitals and the Hf d orbitals contribution at VBM and CBm, respectively are shown in Figure 2[g]. For BaSnS₃, the contribution of S p orbitals at VBM and the hybridization of Sn s and S p orbitals are shown in Figure 2[h]. From the electronic structure, we observe p-d transition in Hf-based perovskites, where as p-p and p-s transition in Sn-based perovskites. Notably, perovskites are well known for their transport

properties. Thus, here we compute the band structures for all the cases (see SI, Fig S1) and their corresponding reduced mass (μ). We observe $\mu < 1$ for all the cases, which in turn indicates high carrier mobility, and therefore infers the better charge carrier transport. However, for BaSnS₃ and SrSnS₃, $m_h^* < m_e^*$ due to the difference in the Sn-S bonding strength at valence band edge (vide supra).

Table 2: Calculated effective mass of electron (m_e^*), hole (m_h^*) and reduced mass (μ) along a Γ –Z high symmetry path. All values are in terms of free-electron mass (m_e).

Configurations	m_e^*	m_h^*	μ
BaHfS ₃	0.367	0.642	0.233
BaSnS ₃	0.639	0.233	0.170
CaHfS ₃	0.444	0.500	0.235
CaSnS ₃	0.385	0.450	0.207
SrHfS ₃	0.445	0.567	0.249
SrSnS ₃	0.527	0.213	0.152

Table 3: Band gap (in eV) of chalcogenide perovskites. i , d , e and t represent indirect, direct, experimental and theoretical band gap.

Configurations	PBE	HSE06	G ₀ W ₀ @PBE	Previous work
BaHfS ₃	1.12	1.97	2.17	2.17 _e ¹⁰
BaSnS ₃	0.87 ⁱ (0.95 ^d)	1.83 ⁱ (1.96 ^d)	1.91 ⁱ (2.03 ^d)	1.62 _t ¹¹
CaHfS ₃	1.38	2.23	2.46	2.21 _t ¹¹
CaSnS ₃	0.76	1.40	1.43	1.58 _t ¹¹
SrHfS ₃	1.47	2.32	2.59	2.41 _e ¹¹
SrSnS ₃	0.96	1.94	2.04	1.56 _t ¹¹

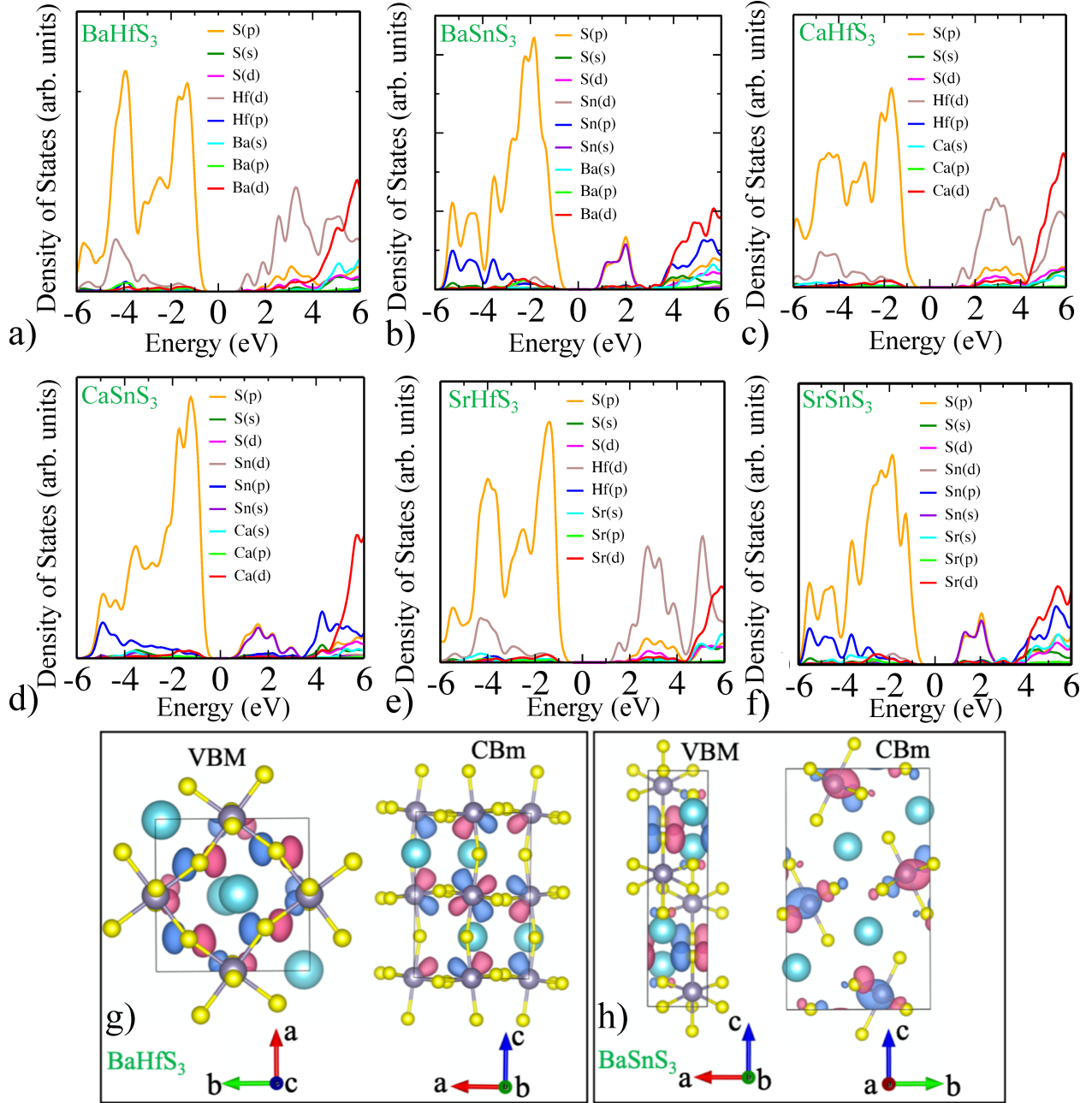


Figure 2: Electronic partial density of states (pDOS) of (a) BaHfS₃, (b) BaSnS₃, (c) CaHfS₃, (d) CaSnS₃, (e) SrHfS₃, (f) SrSnS₃ using HSE06 ϵ_{xc} functional. Wave function analysis in real space of (g) BaHfS₃, and (h) BaSnS₃ at VBM and CBM.

Note that, all the ABS₃ perovskites have band gap less than 2.6 eV, thereby suitable for optoelectronic applications. However, we observe a slight indirect band gap for BaSnS₃ (differ by 0.08 eV), and weakly indirect band gap for SrSnS₃ (differ by few meV's). In other words, the direct gap is at energy level very close to indirect gap. The reason for

indirect band gap could be a large octahedral tilting (BS_6) for needle like phase, indicated from distortion index value given in Table 1. The band gaps computed from semi-local PBE ϵ_{xc} functional are underestimated due to well known self-interaction error (see Table 3). However, hybrid ϵ_{xc} functional HSE06 works very well and correct the band gap i.e. in agreement with the previous reports (see Table 3). This shows the reliability of hybrid functional HSE06 to predict the electronic structure accurately. For optical properties, we go beyond the HSE06, and performed MBPT viz. GW and BSE calculations. GW calculations determine the fundamental band gap analogous to photoelectron spectroscopy (PES) and inverse photoelectron spectroscopy (IPES),^{35,36} and assumed to be more accurate where as BSE calculation predict the optical band gap akin to experimental optical absorption spectroscopy.^{33,34}

The electron-hole interaction is explicitly considered in the BSE calculations.³⁹ Firstly, we perform single shot GW (G_0W_0) on the top of PBE to determine the optical response. Note that the quasiparticle (QP) band gap is slightly overestimated as compare to experimental band gap, due to non-inclusion of electron-hole interaction. Table 3 presents the QP gaps of ABS_3 calculated using GW@PBE. The experimental band gaps are nicely captured from GW calculations, however overestimated from the reported theoretical band gap calculations, as many of them are performed using semi-local or hybrid ϵ_{xc} functionals. This indicates the advantage of performing MBPT calculations and could be very useful for ongoing experimental work. The imaginary part of the dielectric function [$\text{Im}(\epsilon)$] calculated using GW@PBE and BSE@GW@PBE is shown in Figure 3. The oscillator strength corresponding to BSE@GW@PBE is also shown in Figure 3. We compute the exciton binding energy (E_B) by taking the difference of the QP band gap (GW@PBE peak position) and the optical band gap (BSE@GW@PBE peak position). The E_B of the first bright exciton for $BaHfS_3$, $BaSnS_3$, $CaHfS_3$, $CaSnS_3$, $SrHfS_3$ and $SrSnS_3$ is 0.193 eV, 0.134 eV, 0.250 eV, 0.222 eV, 0.256 eV, and 0.148 eV, respectively. From the analysis of BSE eigenvalues, we observe a dark exciton (optically inactive) below the first bright exciton for the case of $BaHfS_3$, $BaSnS_3$, and $SrSnS_3$

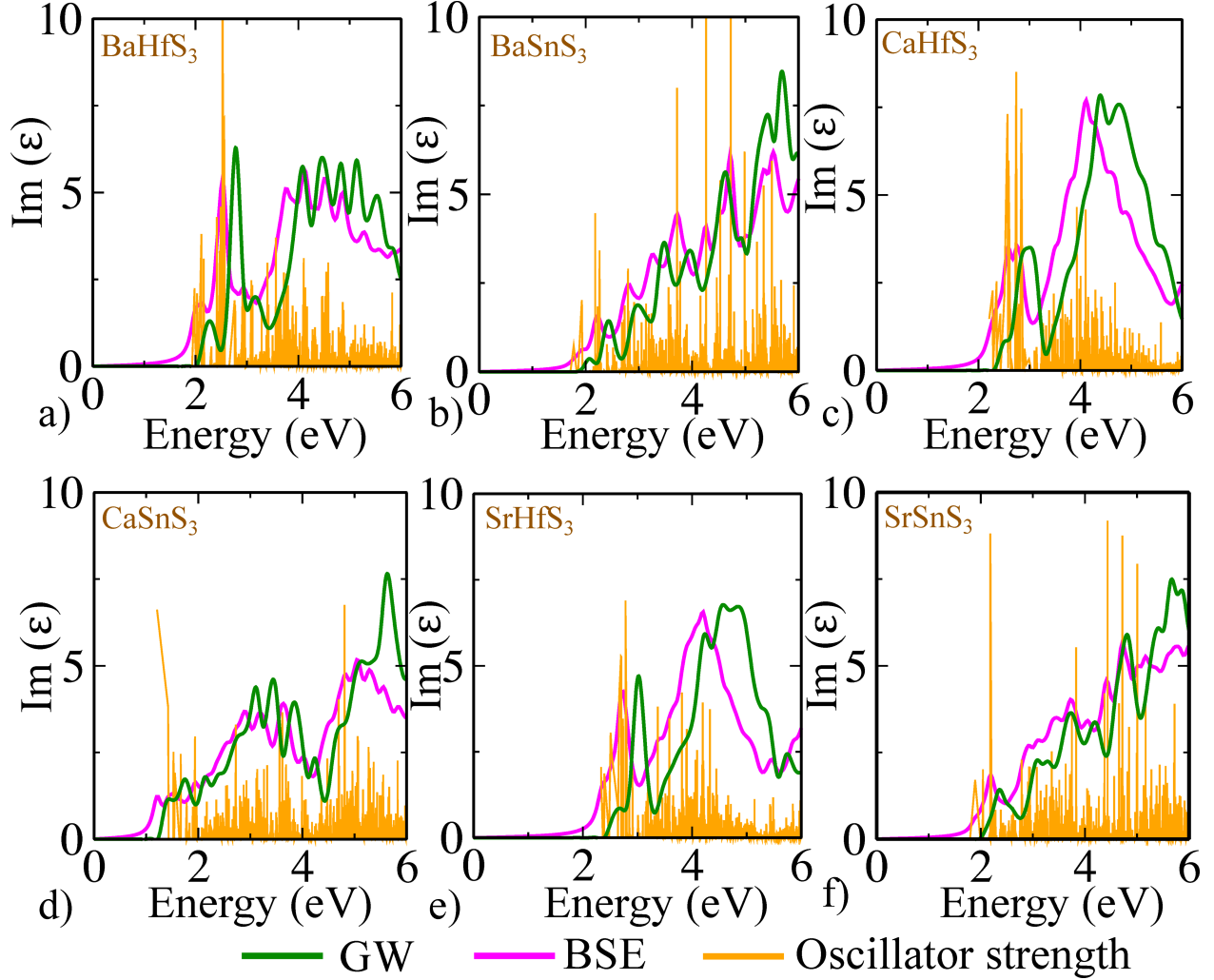


Figure 3: Imaginary $[\text{Im}(\epsilon)]$ part of the dielectric function average along x, y and z directions for (a) BaHfS₃, (b) BaSnS₃, (c) CaHfS₃, (d) CaSnS₃, (e) SrHfS₃, (f) SrSnS₃ obtained using G₀W₀@PBE and BSE@G₀W₀@PBE. The oscillator strength is represented by orange color.

perovskites. The E_B corresponding to the dark excitons are 0.236 eV, 0.316 eV, and 0.248 eV for BaHfS₃, BaSnS₃, and SrSnS₃, respectively. The oscillator strength matches well with the excitonic peak position. The optical transitions below the quasiparticle band gap may lead to various interesting excitonic properties.^{40,41} Using aforementioned quantities such as exciton binding energy, band gap, dielectric function, and reduced mass, we compute several excitonic parameters such as excitonic temperature (T_{exc}), radius (r_{exc}), and probability of wavefunction ($|\phi_n(0)|^2$) for electron-hole pair at zero separation (see details in SI). The inverse of $|\phi_n(0)|^2$ gives a qualitative description of the excitonic lifetime (τ). Therefore,

the exciton lifetime (τ) for the perovskites follows an order: $\text{SrSnS}_3 > \text{BaSnS}_3 > \text{CaSnS}_3 > \text{BaHfS}_3 > \text{CaHfS}_3 > \text{SrHfS}_3$. Hence, we obtain that Sn based chalcogenides have larger exciton lifetime than Hf based chalcogenides. Among Sn-based chalcogenides, needle-like phase show large exciton lifetime than orthorhombic phase.

Table 4: Calculated excitonic parameters for chalcogenide perovskites

Excitonic parameters	BaHfS ₃	BaSnS ₃	CaHfS ₃	CaSnS ₃	SrHfS ₃	SrSnS ₃
E_B (eV)	0.193	0.134	0.250	0.222	0.256	0.148
T_{exc} (K)	2239	1555	2901	2576	2970	1717
r_{exc} (nm)	0.932	1.43	0.841	1.046	0.788	1.667
$ \phi_n(0) ^2(10^{27}\text{m}^{-3})$	0.393	0.108	0.535	0.277	0.649	0.069

We have obtained high E_B values compared to conventional 3D halide perovskite.⁴² This can be explained by the interplay of electronic and ionic contribution to the dielectric screening. Note that, an electronic contribution is dominant over the ionic one, if E_B is much larger than the longitudinal optical phonon energy ($\hbar\omega_{\text{LO}}$).⁴³ In that scenario, ionic contribution can be neglected, and as a result, E_B does not change. Following this, in chalcogenide perovskite cases, all the dominant longitudinal optical active phonon modes are below 50 meV (see Figure 4). Table 4 presents E_B calculated from BSE calculations, where $E_B \gg \hbar\omega_{\text{LO}}$, hence ionic screening to dielectric function can be ignored. Further, we have also employed Wannier-Mott approach to validate the E_B . As per this model, the E_B is dependent on the reduced mass of the charge carriers (μ) for screened Coulomb interacting e-h pairs and the effective dielectric constant (ε_{eff}). The expression is given by:

$$E_B = \frac{\mu}{\varepsilon_{\text{eff}}^2} R_\infty \quad (1)$$

where, R_∞ and ε_{eff} are the Rydberg constant and the value lies in between the static value of electronic and ionic dielectric constants, respectively. The upper and lower bound to the exciton binding energy can be calculated from the contribution of electronic and ionic

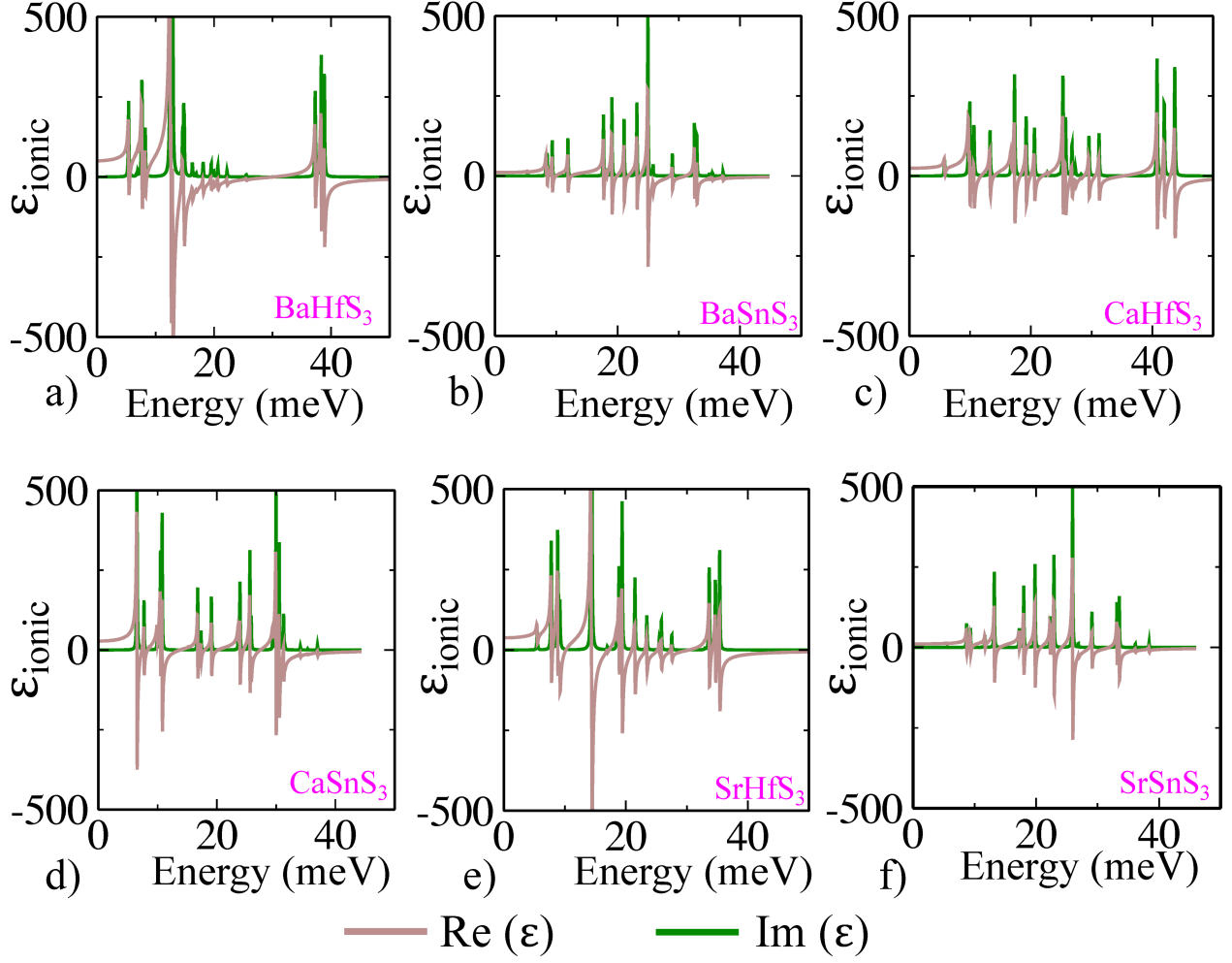


Figure 4: DFPT calculations to determine the ionic contribution to dielectric function for (a) BaHfS₃, (b) BaSnS₃, (c) CaHfS₃, (d) CaSnS₃, (e) SrHfS₃, (f) SrSnS₃.

static dielectric constants. For BaHfS₃, BaSnS₃, CaHfS₃, CaSnS₃, SrHfS₃ and SrSnS₃, the corresponding static electronic dielectric constants are 4.10, 4.60, 3.73, 4.09, 3.71, and 4.79, respectively. Note that, these values are obtained using BSE. The DFPT calculations are performed to determine static ionic dielectric constants i.e. 50.45, 10.77, 24.16, 27.91, 37.76, and 10.94 for respective perovskites (see Figure 4). We notice that the needle-like phase has relatively a low value of static ionic dielectric constants. Using Equation 1, we determine the upper and lower bounds of E_B by substituting reduced mass from Table 2, and the above mentioned static electronic and ionic dielectric constants. We have found that the upper bounds E_B (Table 5) agree well with the difference of GW and BSE peak positions (listed

Table 5: The upper and lower limit of exciton binding energy (E_B) for chalcogenide perovskites

Configurations	Upper bound (eV)	Lower bound (meV)
BaHfS ₃	0.188	1.24
BaSnS ₃	0.149	19.92
CaHfS ₃	0.227	5.47
CaSnS ₃	0.189	3.61
SrHfS ₃	0.230	2.37
SrSnS ₃	0.138	17.27

in Table 4). This confirms that for chalcogenide perovskites, the electronic contribution is dominant over the ionic contribution in dielectric screening.

Further, we have used Fröhlich mesoscopic model^{44,45} to investigate the interaction of longitudinal optical phonon modes with the carriers that strongly influence the carrier mobility. This interaction is defined by the dimensionless Fröhlich parameter α , given by

$$\alpha = \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_{\text{static}}} \right) \sqrt{\frac{R_\infty}{ch\omega_{\text{LO}}}} \sqrt{\frac{m^*}{m_e}} \quad (2)$$

where h and c are Planck's constant and speed of light, respectively. The Fröhlich parameter α is dependent on the ϵ_∞ (electronic dielectric constant), ϵ_{static} (ionic static dielectric constant), carrier effective mass (m^*), and phonon frequency ω_{LO} . The characteristic frequency ω_{LO} has been calculated using athermal 'B' scheme of Hellwarth *et al.*,⁴⁶ where spectral average of infrared active optical phonon modes are considered. The computed α values are listed in Table 6, the α parameter for hole is given in SI. By knowing α , we compute the polaron energy (E_p) using Equation 3. Note that the polaron formation may lead to reduction of quasiparticle energy of electron and hole, and is given by the following equation:^{43,47}

$$E_p = (-\alpha - 0.0123\alpha^2)\hbar\omega_{\text{LO}} \quad (3)$$

For BaHfS₃, BaSnS₃, CaHfS₃, CaSnS₃, SrHfS₃, SrSnS₃, the QP gap is lowered by 0.17, 0.09,

0.21, 0.15, 0.19, 0.08 eV, respectively. By comparing these values with E_B , we obtain that the charge separated polaronic state is less stable than the bound exciton. Other polaron parameters such as effective polaron masses (m_P), radii (l_P) and polaron mobilities (μ_P) are determined using Hellwarth polaron model.⁴⁶ These parameters determine an upper limit for charge carrier mobilities by assuming only the involvement of optical phonons (see details in SI). However, one may expect a lower value of polaron carrier mobility, if local distortions due to polarons and defect scattering due to acoustic phonons are taken into account. From Table 6, we have found that large polarons (l_P) are formed, and Sn-based chalcogenides possess a large value of polaron mobility than Hf based ones.

Table 6: Polaron parameters for electrons in chalcogenide perovskites

Configurations	$1/\epsilon^*$	ω_{LO} (cm^{-1})	α_e	m_P	l_P ($\text{\AA}$)	μ_P ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)
BaHfS ₃	0.223	148.53	3.68	0.76	35.75	15.82
BaSnS ₃	0.124	195.32	2.36	1.05	55.26	16.41
CaHfS ₃	0.226	253.92	3.13	0.976	57.96	13.84
CaSnS ₃	0.208	167.54	3.31	0.766	41.36	17.01
SrHfS ₃	0.242	158.47	4.26	1.10	34.71	9.58
SrSnS ₃	0.117	199.23	1.99	0.80	61.06	25.08

Notably, ABS₃ perovskites can be considered as good solar absorbers as they exhibit large absorption coefficient and most of them show a direct band gap in visible region range. Therefore, to quantify this, we choose a parameter introduced by Yu *et al.* known as spectroscopic limited maximum efficiency (SLME).^{37,48} SLME determines the maximum limit of the solar power conversion efficiency of an absorber material. It incorporates the shape of absorption spectra, band gap and its nature (direct or indirect), thickness of the thin film absorber layer and the material dependent non-radiative recombination losses. This is considered as an improved version of Shockley and Queisser (SQ) efficiency.⁴⁹ From above discussion we know that SLME depends on the nature of the band gap, however for various perovskites,⁵⁰ it has been seen that even after having a direct electronic band gap, the optical allowed dipole transition from VBM to CBm was forbidden. This happens because of

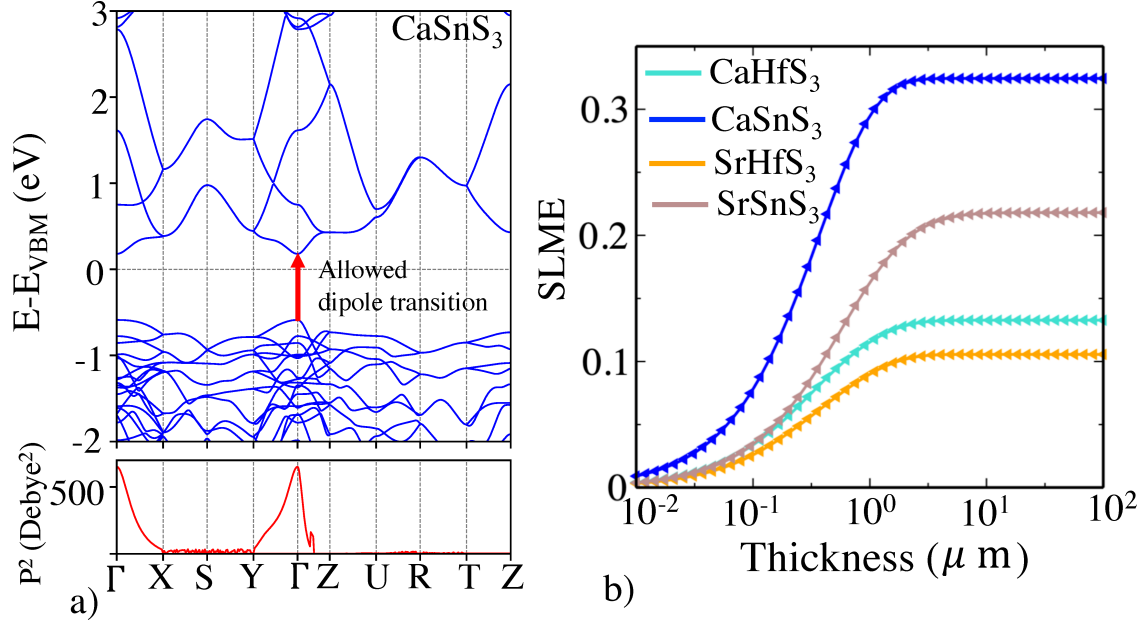


Figure 5: Electronic band structure and transition probability from VBM to CBm (square of dipole transition matrix elements) for CaSnS_3 . Spectroscopic limited maximum efficiency of ABS_3 ($\text{A}=\text{Ca}$, Sr , and $\text{B}=\text{Hf}$, Sn).

the presence of inversion symmetry that leads to VBM and CBm at the same parity. We, therefore, check the possibility of the optical transition from VBM to CBm for our systems. For this, we calculate the dipole transition matrix, defined as the electric dipole moment related with a transition between the initial state and the final state. Its square gives the probability of transition between the two states. We have computed the square of the dipole transition matrix elements (p^2) for all the systems. We have found that BaHfS_3 has forbidden dipole transition at Γ , regardless of direct electronic band gap (see SI, Fig S1). Figure 5, shows an optically allowed dipole transition for CaSnS_3 perovskites (for other configurations, see SI, Fig S1). Thus, keeping this in mind, we proceed next for SLME calculations, only for systems, that possesses direct band gap along with optically allowed dipole transitions. Note that, SrSnS_3 has also been considered, as the difference of indirect and direct band gap of only few meV's, that does not impact the absorption coefficient. For SLME, the input parameters are band gap, thickness, absorption coefficient and the standard solar spectrum. Figure 5 presents the calculated SLME of ABS_3 ($\text{A}=\text{Ca}$, Sr , and $\text{B}=\text{Hf}$, Sn). SLME values

at 10 μm absorber layer thickness are 13.26%, 32.45%, 10.56%, and 21.80% for CaHfS_3 , CaSnS_3 , SrHfS_3 , SrSnS_3 respectively (see Figure 5). We have achieved the highest value of SLME for CaSnS_3 , that could serve as a best material for photovoltaic applications.

In summary, we have determined the electronic, optical (excitonic and polaronic) properties of chalcogenide perovskites ABS_3 ($\text{A} = \text{Ba, Ca, Sr}$, and $\text{B} = \text{Hf, Sn}$) under the framework of DFT and MBPT. We have obtained reduce mass, $\mu < 1$ for all the cases, that confirms high carrier mobility. For BaSnS_3 and SrSnS_3 , the difference in Sn-S bonding strength of SnS_6 octahedra leads to lighter valence bands, which in turn boost up the hole mobility. The large value of exciton binding energy is noted for chalcogenide perovskites i.e., 0.193, 0.134, 0.250, 0.222, 0.256, and 0.148 eV for BaHfS_3 , BaSnS_3 , CaHfS_3 , CaSnS_3 , SrHfS_3 and SrSnS_3 , respectively. The exciton binding energy computed from BSE calculations are well in agreement with Wannier-Mott approach, thereby indicate that electronic contribution is dominant over ionic contribution in dielectric screening. Further, from Fröhlich's mesoscopic model, we have found that the charge-separated polaronic states are less stable than the bound excitons. Lastly, the spectroscopic limited maximum efficiency (SLME) suggest that among all studied chalcogenide perovskites, CaSnS_3 could be a best choice for efficient photovoltaic applications.

Computational Methods

The DFT^{29,30} calculations are performed as implemented in the Vienna *ab initio* simulation package (VASP).^{51,52} Projector-augmented wave (PAW) pseudopotentials^{52,53} are used to describe the ion-electron interactions. The valence states considered for Ca, Sr, Ba, Hf, Sn and S are $3s^2 3p^6 4s^2$, $4s^2 4p^6 5s^2$, $5s^2 5p^6 6s^2$, $5p^6 6s^2 6d^4$, $4d^{10} 5s^2 5p^2$, and $3s^2 3p^4$, respectively. PBE³¹ exchange-correlation (ϵ_{xc}) functional has been used for the structural optimization. The structural relaxation are performed until the forces are smaller than 0.001 eV/Å. The plane wave basis set expansion or kinetic energy cutoff is set to 500 eV. For single point energy

calculations, the tolerance criteria for energy convergence is set to 0.001 meV. For Brillouin zone integration, a k -grid of $7 \times 7 \times 5$ is used, generated from Monkhorst-Pack⁵⁴ scheme. The advanced hybrid ϵ_{xc} functional HSE06³² and GW calculations are performed for the better estimation of the electronic band gap. To determine excitonic properties, Bethe-Salpeter equation (BSE)^{33,34} calculations are performed on top of single shot GW^{35,36} (G_0W_0). PBE ϵ_{xc} functional is considered as a starting point for single shot GW calculations. A grid of 50 frequency points is used for the polarizability calculations. We have considered sufficient number of unoccupied bands i.e. nine times the number of occupied bands. The convergence for number of unoccupied bands is shown in SI. For BSE calculations, Γ -centered $3 \times 3 \times 2$ k -grid has been used. The electron-hole kernel for BSE calculations are constructed by 24 occupied and 24 unoccupied bands (for convergence see SI). Density functional perturbation theory (DFPT) calculations are performed to get the ionic contribution to dielectric screening using $7 \times 7 \times 5$ k -grid. Note that spin-orbit coupling (SOC) has not been taken into account, as it does not alter the electronic structure (see SI).

Acknowledgement

PB acknowledges UGC, India, for the senior research fellowship [grant no. 20/12/2015 (ii) EUV]. SB acknowledges the financial support from SERB under core research grant (grant no. CRG/2019/000647). We acknowledge the High Performance Computing (HPC) facility at IIT Delhi for computational resources.

Supporting Information Available

(I) Electronic band structure and transition probability. (II) Effect of spin-orbit coupling on band gap. (III) Convergence of number of bands used in single shot GW calculations. (IV) Convergence of number of occupied (NO) and unoccupied bands (NV) used in electron-hole interaction kernel for BSE calculations. (V) Excitonic parameters: exciton binding energy

(E_B), dielectric constant (ϵ_{eff}), band gap (E_g) and reduced mass (μ). (VI) Polaron parameters of chalcogenide perovskites. (VII) pDOS of S atoms of chalcogenide perovskites.

References

- (1) Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells. *Journal of the American Chemical Society* **2009**, *131*, 6050–6051.
- (2) National Renewable Energy Laboratory (NREL) Best Research-Cell Efficiency Chart. <https://www.nrel.gov/pv/cell-efficiency.html>, accessed: January 26, 2021.
- (3) Babayigit, A.; Ethirajan, A.; Muller, M.; Conings, B. Toxicity of organometal halide perovskite solar cells. *Nature materials* **2016**, *15*, 247–251.
- (4) Basera, P.; Kumar, M.; Saini, S.; Bhattacharya, S. Reducing lead toxicity in the methylammonium lead halide MAPbI₃: Why Sn substitution should be preferred to Pb vacancy for optimum solar cell efficiency. *Phys. Rev. B* **2020**, *101*, 054108.
- (5) Kuhar, K.; Crovetto, A.; Pandey, M.; Thygesen, K. S.; Seger, B.; Vesborg, P. C.; Hansen, O.; Chorkendorff, I.; Jacobsen, K. W. Sulfide perovskites for solar energy conversion applications: computational screening and synthesis of the selected compound LaYS 3. *Energy & Environmental Science* **2017**, *10*, 2579–2593.
- (6) Tiwari, D.; Hutter, O. S.; Longo, G. Chalcogenide perovskites for photovoltaics: current status and prospects. *Journal of Physics: Energy* **2021**, *3*, 034010.
- (7) Lelieveld, R.; IJdo, D. J. W. Sulphides with the GdFeO₃ structure. *Acta Crystallographica Section B* **1980**, *36*, 2223–2226.
- (8) Lee, C.-S.; Klenke, K. M.; Klenke, H. Synthesis, structure, and electronic and physical properties of the two SrZrS₃ modifications. *Solid State Sciences* **2005**, *7*, 1049 – 1054.

- (9) Meng, W.; Saparov, B.; Hong, F.; Wang, J.; Mitzi, D. B.; Yan, Y. Alloying and Defect Control within Chalcogenide Perovskites for Optimized Photovoltaic Application. *Chemistry of Materials* **2016**, *28*, 821–829.
- (10) Perera, S.; Hui, H.; Zhao, C.; Xue, H.; Sun, F.; Deng, C.; Gross, N.; Milleville, C.; Xu, X.; Watson, D. F. et al. Chalcogenide Perovskites – An Emerging Class of Ionic Semiconductors. *Nano Energy* **2016**, *22*, 129 – 135.
- (11) Niu, S.; Huyan, H.; Liu, Y.; Yeung, M.; Ye, K.; Blankemeier, L.; Orvis, T.; Sarkar, D.; Singh, D. J.; Kapadia, R. et al. Bandgap Control via Structural and Chemical Tuning of Transition Metal Perovskite Chalcogenides. *Advanced Materials* **2017**, *29*, 1604733.
- (12) Comparotto, C.; Davydova, A.; Ericson, T.; Riekehr, L.; Moro, M. V.; Kubart, T.; Scragg, J. Chalcogenide Perovskite BaZrS₃: Thin Film Growth by Sputtering and Rapid Thermal Processing. *ACS Applied Energy Materials* **2020**, *3*, 2762–2770.
- (13) Wei, X.; Hui, H.; Perera, S.; Sheng, A.; Watson, D. F.; Sun, Y.-Y.; Jia, Q.; Zhang, S.; Zeng, H. Ti-Alloying of BaZrS₃ Chalcogenide Perovskite for Photovoltaics. *ACS Omega* **2020**, *5*, 18579–18583.
- (14) Ravi, V. K.; Yu, S. H.; Rajput, P. K.; Nayak, C.; Bhattacharyya, D.; Chung, D. S.; Nag, A. Colloidal BaZrS₃ chalcogenide perovskite nanocrystals for thin film device fabrication. *Nanoscale* **2021**, *13*, 1616–1623.
- (15) Kuhar, K.; Crovetto, A.; Pandey, M.; Thygesen, K. S.; Seger, B.; Vesborg, P. C. K.; Hansen, O.; Chorkendorff, I.; Jacobsen, K. W. Sulfide Perovskites for Solar Energy Conversion Applications: Computational Screening and Synthesis of the Selected Compound LaYS₃. *Energy Environ. Sci.* **2017**, *10*, 2579–2593.
- (16) Vonrüti, N.; Aschauer, U. Band-gap engineering in AB(O_xS_{1-x})₃ perovskite oxysulfides: a route to strongly polar materials for photocatalytic water splitting. *J. Mater. Chem. A* **2019**, *7*, 15741–15748.

- (17) Eya, H. I.; Ntsoenzok, E.; Dzade, N. Y. First-Principles Investigation of the Structural, Elastic, Electronic, and Optical Properties of α - and β -SrZrS₃: Implications for Photovoltaic Applications. *Materials* **2020**, *13*.
- (18) Li, W.; Niu, S.; Zhao, B.; Haiges, R.; Zhang, Z.; Ravichandran, J.; Janotti, A. Band gap evolution in Ruddlesden-Popper phases. *Phys. Rev. Materials* **2019**, *3*, 101601.
- (19) Perera, S.; Hui, H.; Zhao, C.; Xue, H.; Sun, F.; Deng, C.; Gross, N.; Milleville, C.; Xu, X.; Watson, D. F. et al. Chalcogenide perovskites—an emerging class of ionic semiconductors. *Nano Energy* **2016**, *22*, 129–135.
- (20) Niu, S.; Huyan, H.; Liu, Y.; Yeung, M.; Ye, K.; Blankemeier, L.; Orvis, T.; Sarkar, D.; Singh, D. J.; Kapadia, R. et al. Bandgap control via structural and chemical tuning of transition metal perovskite chalcogenides. *Advanced Materials* **2017**, *29*, 1604733.
- (21) Meng, W.; Saparov, B.; Hong, F.; Wang, J.; Mitzi, D. B.; Yan, Y. Alloying and defect control within chalcogenide perovskites for optimized photovoltaic application. *Chemistry of Materials* **2016**, *28*, 821–829.
- (22) Sun, Y.-Y.; Agiorgousis, M. L.; Zhang, P.; Zhang, S. Chalcogenide perovskites for photovoltaics. *Nano letters* **2015**, *15*, 581–585.
- (23) Kumar, M.; Singh, A.; Gill, D.; Bhattacharya, S. Optoelectronic Properties of Chalcogenide Perovskites by Many-Body Perturbation Theory. *The Journal of Physical Chemistry Letters* **2021**, *12*, 5301–5307.
- (24) Li, Z.; Xie, H.; Xia, Y.; Hao, S.; Pal, K.; Kanatzidis, M. G.; Wolverton, C.; Tang, X. Weak-Bonding Elements Lead to High Thermoelectric Performance in BaSnS₃ and SrSnS₃: A First-Principles Study. *Chemistry of Materials* **2022**,
- (25) Hanzawa, K.; Iimura, S.; Hiramatsu, H.; Hosono, H. Material design of green-light-

- emitting semiconductors: Perovskite-type sulfide SrHfS_3 . *Journal of the American Chemical Society* **2019**, *141*, 5343–5349.
- (26) Shaili, H.; Beraich, M.; Ouafi, M.; mehdi Salmani, E.; Essajai, R.; Battal, W.; Rouchdi, M.; Taibi, M.; Hassanain, N.; Mzerd, A. et al. Synthesis of the Sn-based CaSnS_3 chalcogenide perovskite thin film as a highly stable photoabsorber for optoelectronic applications. *Journal of Alloys and Compounds* **2021**, *851*, 156790.
- (27) Miyata, K.; Zhu, X.-Y. Ferroelectric large polarons. *Nature materials* **2018**, *17*, 379–381.
- (28) Poncé, S.; Schlipf, M.; Giustino, F. Origin of low carrier mobilities in halide perovskites. *ACS Energy Letters* **2019**, *4*, 456–463.
- (29) Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas. *Phys. Rev.* **1964**, *136*, B864–B871.
- (30) Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **1965**, *140*, A1133–A1138.
- (31) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- (32) Krukau, A. V.; Vydrov, O. A.; Izmaylov, A. F.; Scuseria, G. E. Influence of the exchange screening parameter on the performance of screened hybrid functionals. *The Journal of Chemical Physics* **2006**, *125*, 224106.
- (33) Albrecht, S.; Reining, L.; Del Sole, R.; Onida, G. Ab Initio Calculation of Excitonic Effects in the Optical Spectra of Semiconductors. *Phys. Rev. Lett.* **1998**, *80*, 4510–4513.
- (34) Rohlfing, M.; Louie, S. G. Electron-Hole Excitations in Semiconductors and Insulators. *Phys. Rev. Lett.* **1998**, *81*, 2312–2315.

- (35) Hedin, L. New Method for Calculating the One-Particle Green’s Function with Application to the Electron-Gas Problem. *Phys. Rev.* **1965**, *139*, A796–A823.
- (36) Hybertsen, M. S.; Louie, S. G. First-Principles Theory of Quasiparticles: Calculation of Band Gaps in Semiconductors and Insulators. *Phys. Rev. Lett.* **1985**, *55*, 1418–1421.
- (37) Yu, L.; Zunger, A. Identification of Potential Photovoltaic Absorbers Based on First-Principles Spectroscopic Screening of Materials. *Phys. Rev. Lett.* **2012**, *108*, 068701.
- (38) Yamaoka, S.; Okai, B. Preparations of BaSnS₃, SrSnS₃ and PbSnS₃ at high pressure. *Materials Research Bulletin* **1970**, *5*, 789–794.
- (39) Biswas, T.; Ravindra, P.; Athresh, E.; Ranjan, R.; Avasthi, S.; Jain, M. Optical Properties of Zn₂Mo₃O₈: Combination of Theoretical and Experimental Study. *The Journal of Physical Chemistry C* **2017**, *121*, 24766–24773.
- (40) Basera, P.; Singh, A.; Gill, D.; Bhattacharya, S. Capturing excitonic and polaronic effects in lead iodide perovskites using many-body perturbation theory. *Journal of Materials Chemistry C* **2021**, *9*, 17113–17123.
- (41) Jain, M.; Gill, D.; Bhumla, P.; Basera, P.; Bhattacharya, S. Theoretical insights to excitonic effect in lead bromide perovskites. *Applied Physics Letters* **2021**, *118*, 192103.
- (42) Herz, L. M. How Lattice Dynamics Moderate the Electronic Properties of Metal-Halide Perovskites. *The Journal of Physical Chemistry Letters* **2018**, *9*, 6853–6863.
- (43) Bokdam, M.; Sander, T.; Stroppa, A.; Picozzi, S.; Sarma, D. D.; Franchini, C.; Kresse, G. Role of polar phonons in the photo excited state of metal halide perovskites. *Scientific reports* **2016**, *6*, 1–8.
- (44) Sendner, M.; Nayak, P. K.; Egger, D. A.; Beck, S.; Müller, C.; Epding, B.; Kowalsky, W.; Kronik, L.; Snaith, H. J.; Pucci, A. et al. Optical phonons in methylammonium

- lead halide perovskites and implications for charge transport. *Mater. Horiz.* **2016**, *3*, 613–620.
- (45) Frost, J. M. Calculating polaron mobility in halide perovskites. *Phys. Rev. B* **2017**, *96*, 195202.
- (46) Hellwarth, R. W.; Biaggio, I. Mobility of an electron in a multimode polar lattice. *Phys. Rev. B* **1999**, *60*, 299–307.
- (47) Franchini, C.; Reticcioli, M.; Setvin, M.; Diebold, U. Polarons in materials. *Nature Reviews Materials* **2021**, 1–27.
- (48) A Python3 Implementation of the Spectroscopic Limited Maximum Efficiency (SLME) Analysis of Solar Absorbers. <https://github.com/ldwillia/SL3ME>, accessed: January 12, 2021.
- (49) Shockley, W.; Queisser, H. J. Detailed Balance Limit of Efficiency of p-n Junction Solar Cells. *Journal of Applied Physics* **1961**, *32*, 510–519.
- (50) Kangsabanik, J.; Sugathan, V.; Yadav, A.; Yella, A.; Alam, A. Double perovskites overtaking the single perovskites: A set of new solar harvesting materials with much higher stability and efficiency. *Physical Review Materials* **2018**, *2*, 055401.
- (51) Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Computational Materials Science* **1996**, *6*, 15 – 50.
- (52) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **1999**, *59*, 1758–1775.
- (53) Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **1994**, *50*, 17953–17979.
- (54) Monkhorst, H. J.; Pack, J. D. Special points for Brillouin-zone integrations. *Phys. Rev. B* **1976**, *13*, 5188–5192.

Chalcogenide perovskites: an emerging class of semiconductors for optoelectronics

Pooja Basera* and Saswata Bhattacharya*

Department of Physics, Indian Institute of Technology Delhi, New Delhi, India

E-mail: Pooja.Basera@physics.iitd.ac.in[PB]; saswata@physics.iitd.ac.in[SB]

Phone: +91-11-2659 1359

Supplemental Material

- I.** Electronic band structure and transition probability
- II.** Effect of spin-orbit coupling on band gap
- III.** Convergence of number of bands used in single shot GW calculations
- IV.** Convergence of number of occupied (NO) and unoccupied bands (NV) used in electron-hole interaction kernel for BSE calculations
- V.** Excitonic parameters: exciton binding energy (E_B), dielectric constant (ϵ_{eff}), band gap (E_g) and reduced mass (μ)
- VI.** Polaron parameters of chalcogenide perovskites
- VII.** pDOS of S atoms of chalcogenide perovskites

I. Electronic band structure and transition probability

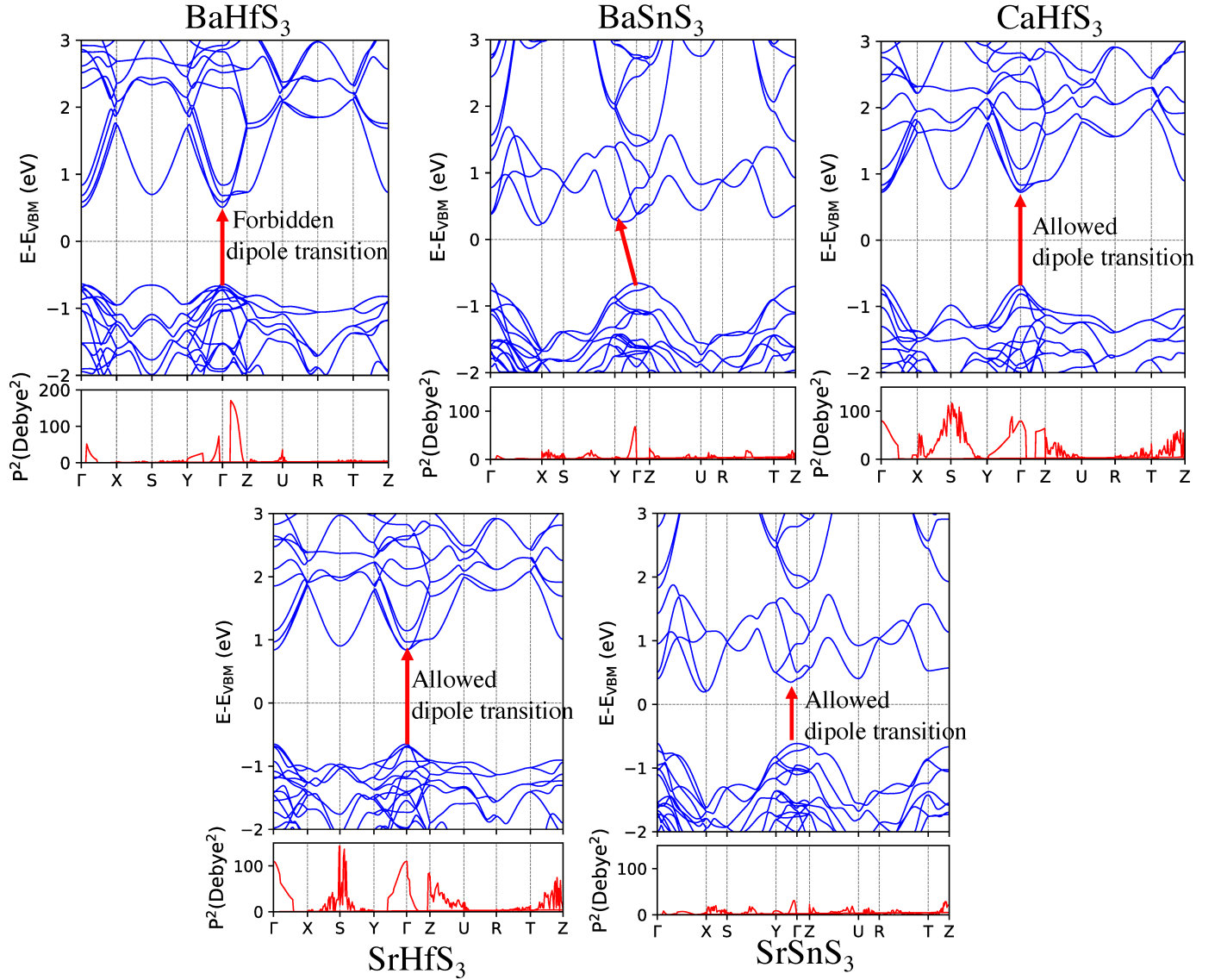


Figure S1: Electronic band structure and transition probability from VBM to CBm (square of dipole transition matrix elements) using PBE ϵ_{xc} functional. BaHfS₃ has forbidden dipole transition at Γ point.

II. Effect of spin-orbit coupling on band gap

Table S1: Band gap of BaHfS₃, BaSnS₃, CaHfS₃, CaSnS₃, SrHfS₃, and SrSnS₃ using PBE ϵ_{xc} functional.

Configurations	Without SOC (eV)	With SOC (eV)
BaHfS ₃	1.12	1.03
BaSnS ₃	0.87 (0.95)	0.86 (0.94)
CaHfS ₃	1.38	1.31
CaSnS ₃	0.76	0.79
SrHfS ₃	1.47	1.37
SrSnS ₃	0.96	0.95

III. Convergence of number of bands used in single shot

GW calculations

Table S2: Band gap (in eV) of BaHfS₃ using single shot GW@PBE with different number of bands.

Number of bands	BaHfS ₃
320	2.19
480	2.16
640	2.17
720	2.17
800	2.17

Table S2 shows that 640 bands are sufficient for the calculations. For our calculations, we have used 720 number of occupied bands and 500 eV plane wave energy cutoff.

IV. Convergence of number of occupied (NO) and unoccupied bands (NV) used in electron-hole interaction kernel for BSE calculations

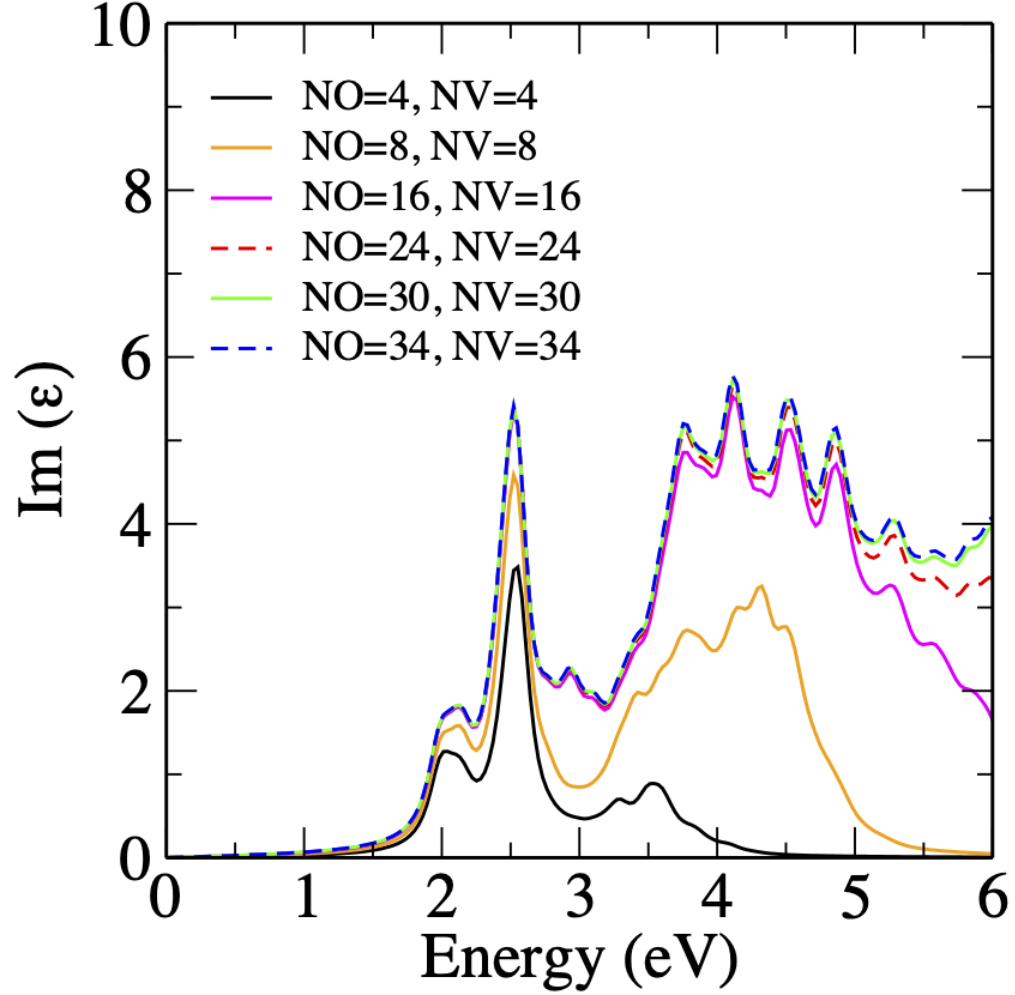


Figure S2: Imaginary part of electronic dielectric function for BaHfS_3 with different number of valence (NO) and conduction bands (NV) used in electron-hole interaction kernel.

From Fig S2, we observe that the imaginary part of the dielectric function is converged for NO=Nv=16 bands. We have used NO=Nv=24 bands in our calculations.

V. Excitonic parameters: exciton binding energy (E_B), dielectric constant (ϵ_{eff}), band gap (E_g) and reduced mass (μ)

The thermal energy needed to separate the exciton is given by:¹

$$T_{\text{exc}} = \frac{E_B}{k_B} \quad (1)$$

where E_B and k_B are the exciton binding energy and the Boltzmann constant, respectively.

The exciton radius with the orbital n is given by:

$$r_{\text{exc}} = \frac{m_0}{\mu} \epsilon_{\text{eff}} n^2 r_{\text{Ry}} \quad (2)$$

where, $r_{\text{Ry}} = 0.0529$ nm is the Bohr radius. m_0 and μ are the free electron mass and reduced mass. ϵ_{eff} is defined as an intermediate value between the static electronic and ionic dielectric constant. In our case, we have considered electronic dielectric constant, since electronic contribution is dominant over ionic contribution in the dielectric screening. The inverse of probability of wave function for e-h pair at zero separation ($|\phi_n(0)|^2$) gives a qualitative description of the excitonic lifetime (τ). The $|\phi_n(0)|^2$ is given by:

$$|\phi_n(0)|^2 = \frac{1}{\pi (r_{\text{exc}})^3 n^3} \quad (3)$$

VI. Polaron parameters of chalcogenide perovskites

“Frohlich’s mesoscopic model” is used to investigate the electron–phonon interaction in our system. In 1954, Frohlich introduced an interaction parameter that describes theoretically the motion of an electron in the vicinity of polar lattice vibration. This parameter is a

Table S3: Electron-phonon coupling parameters for holes in chalcogenides perovskites

Configurations	α_h
BaHfS ₃	4.87
BaSnS ₃	1.42
CaHfS ₃	3.32
CaSnS ₃	3.57
SrHfS ₃	4.81
SrSnS ₃	1.27

dimensionless quantity known as Frohlich coupling constant.^{2,3}

$$\alpha = \frac{1}{\epsilon^*} \sqrt{\frac{R_y}{ch\omega_{LO}}} \sqrt{\frac{m^*}{m_e}} \quad (4)$$

where coupling constant α quantifies the strength of electron-phonon coupling. m^* , m_e , h and c are the effective mass of electron, rest mass of the electron, Planck's constant, and speed of light, respectively. ω_{LO} (in $[\text{cm}^{-1}]$ units) is the optical phonon frequency, $1/\epsilon^*$ is the ionic screening parameter ($1/\epsilon^* = 1/\epsilon_\infty - 1/\epsilon_{\text{static}}$ where, ϵ_{static} and ϵ_∞ are static and high frequency dielectric constant) and R_y is the Rydberg energy.

Further, Feynman extended the Frohlich's polaron theory so that the effective mass of polaron⁴ (m_P) can be calculated using the given equation.³

$$m_P = m^* \left(1 + \frac{\alpha}{6} + \frac{\alpha^2}{40} + \dots \right) \quad (5)$$

where m^* is the effective mass computed from GW band structure calculations. This expression shows that polaron mass is always higher than the effective mass calculated from band structure calculations, thereby influencing charge carrier mobilities.

Further, we have determined the polaron radii⁵ using the following equation:

$$l_P = \sqrt{\frac{h}{2cm^*\omega_{LO}}} \quad (6)$$

Note that, these polaron parameters are used to estimate an upper limit for charge carrier mobilities μ , assuming that only optical phonons are involved.

Hellwarth polaron model⁶ is used to define the polaron mobility:⁷

$$\mu_P = \frac{(3\sqrt{\pi}e)}{2\pi c\omega_{LO}m^*\alpha} \frac{\sinh(\beta/2)}{\beta^{5/2}} \frac{w^3}{v^3} \frac{1}{K} \quad (7)$$

where, $\beta = \hbar c \omega_{LO}/k_B T$, e is the electronic charge, m^* is the effective mass of charge carrier, w and v correspond to temperature dependent variational parameters. K is a function of v , w , and β ⁶ i.e., defined as follows:

$$K(a, b) = \int_0^\infty du [u^2 + a^2 - b \cos(vu)]^{-3/2} \cos(u) \quad (8)$$

Here, a^2 and b are calculated as:

$$a^2 = (\beta/2)^2 + \frac{(v^2 - w^2)}{w^2 v} \beta \coth(\beta v/2) \quad (9)$$

$$b = \frac{(v^2 - w^2)}{w^2 v} \frac{\beta}{\sinh(\beta v/2)} \quad (10)$$

From the following expressions, we have determined the polaron parameters for chalcogenides perovskites.

VII. pDOS of S atoms of chalcogenide perovskites

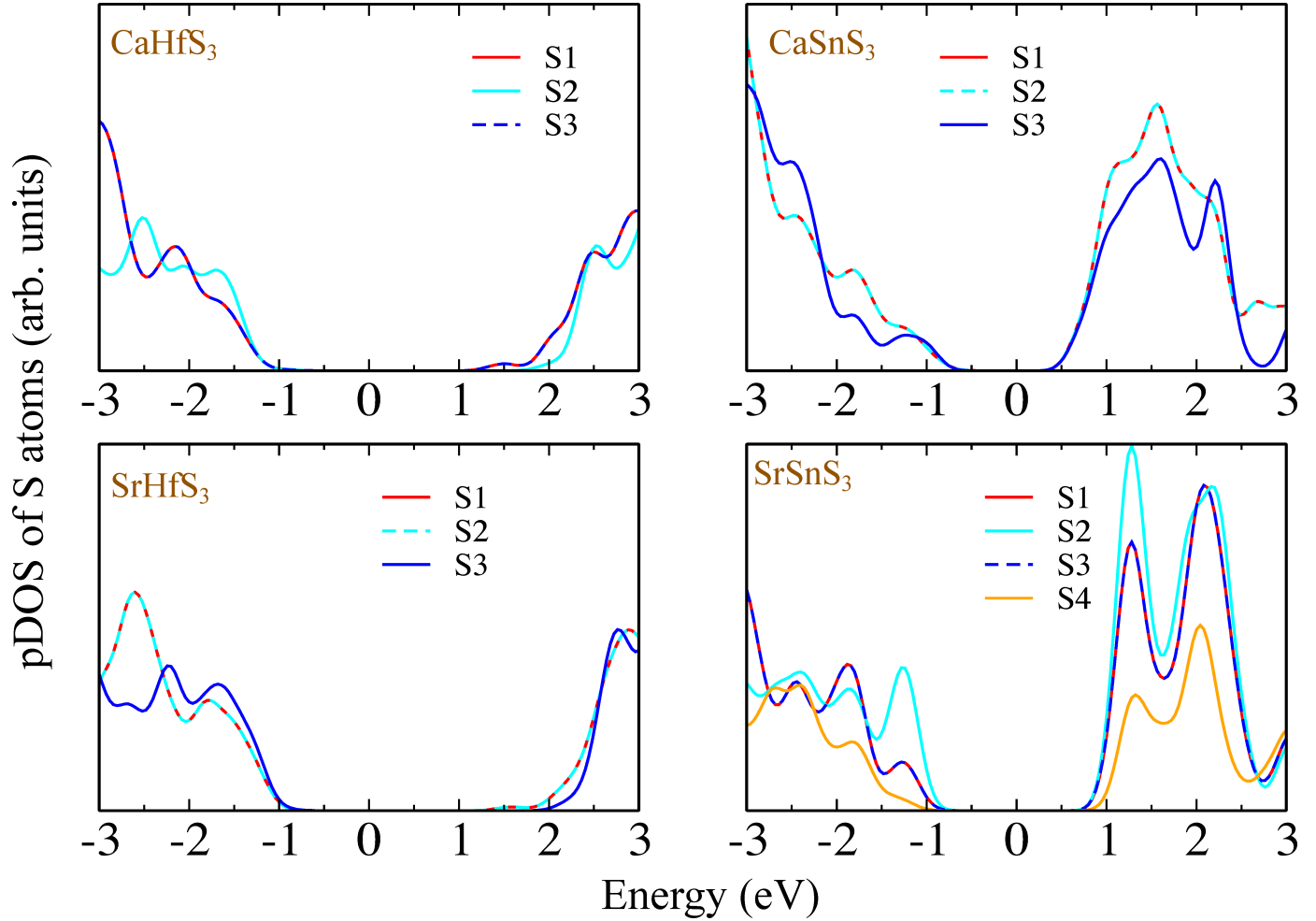


Figure S3: Sulphur atom projected density of states for CaHfS₃, CaSnS₃, SrHfS₃, and SrSnS₃.

References

- (1) Basera, P.; Singh, A.; Gill, D.; Bhattacharya, S. Capturing excitonic and polaronic effects in lead iodide perovskites using many-body perturbation theory. *Journal of Materials Chemistry C* **2021**, *9*, 17113–17123.
- (2) Fröhlich, H. Electrons in lattice fields. *Advances in Physics* **1954**, *3*, 325–361.

- (3) Feynman, R. P.; Hellwarth, R. W.; Iddings, C. K.; Platzman, P. M. Mobility of slow electrons in a polar crystal. *Physical Review* **1962**, *127*, 1004.
- (4) Feynman, R. P. Slow electrons in a polar crystal. *Physical Review* **1955**, *97*, 660.
- (5) Sendner, M.; Nayak, P. K.; Egger, D. A.; Beck, S.; Müller, C.; Epding, B.; Kowalsky, W.; Kronik, L.; Snaith, H. J.; Pucci, A. et al. Optical phonons in methylammonium lead halide perovskites and implications for charge transport. *Materials Horizons* **2016**, *3*, 613–620.
- (6) Hellwarth, R. W.; Biaggio, I. Mobility of an electron in a multimode polar lattice. *Physical Review B* **1999**, *60*, 299.
- (7) Frost, J. M. Calculating polaron mobility in halide perovskites. *Physical Review B* **2017**, *96*, 195202.