Assessing carrier mobility, dopability, and defect tolerance in the chalcogenide perovskite BaZrS$_3$

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Abstract

The chalcogenide perovskite BaZrS$_3$ has attracted much attention as a promising solar absorber for thin-film photovoltaics. Here, we use first-principles calculations to evaluate its carrier transport and defect properties. We find that BaZrS$_3$ has a phonon-limited electron mobility of 37 cm^2/Vs comparable to that in halide perovskites but lower hole mobility of 11 cm^2/Vs. The defect computations indicate that BaZrS$_3$ is intrinsically n-type due to shallow sulfur vacancies, but that strong compensation by sulfur vacancies will prevent attempts to make it p-type. We also establish that BaZrS$_3$ is a defect-tolerant absorber with few low formation energy, deep intrinsic defects. Among the deep defects, sulfur interstitials are the

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strongest nonradiative recombination centers which in sulfur-rich conditions would limit the carrier lifetime to 10 ns. Our work highlights the material's intrinsic limitations in carrier mobility and suggests suppressing the formation of sulfur interstitials to reach long carrier lifetime.

Introduction

Lead halide perovskites have revolutionized the field of photovoltaics (PV) by opening a promising path to earth-abundant, easily processable, and high-efficiency thin-film technologies.[1,2] The exceptional PV performance of halide perovskites is however shadowed by their poor stability.[3] Structural analogy has motivated the search for alternative solar absorbers forming in the perovskite structure but in chemistries that could be more stable.[4–13] The chalcogenide perovskites ABX_3 (A=Ca, Sr, Ba, B=Ti, Zr, and X=S, Se) have emerged in this context with their first suggestion as solar absorbers coming from first-principles studies[4] followed by experimental synthesis and characterization especially of $BaZrS_3$.[14–18] $BaZrS_3$ shows excellent stability in ambient conditions and exhibits a $\sim$1.8 eV direct band gap which can be tuned to 1.5 eV by alloying with $BaTiS_3$ or $BaZrSe_3$.[14,16–23] Significant efforts have been dedicated to growing high-quality thin films of $BaZrS_3$ and its alloys, using a range of techniques such as pulsed laser deposition,[24–26] sputtering,[20,27,28] molecular beam epitaxy,[29,30] and solution-based synthesis.[31–33] Very recently, a proof-of-concept $BaZrS_3$ solar cell has been reported, demonstrating an efficiency of 0.11%.[34] Interestingly, $BaZrS_3$ also stands out as a top candidate in a few high-throughput computational screening of thin-film solar absorbers.[10,35–37]

In this letter, we use first-principles calculations to clarify the carrier transport and defect properties in $BaZrS_3$. We compute the phonon-limited carrier mobility showing that $BaZrS_3$ has intrinsically low hole mobility. We also perform state-of-the-art hybrid-functional defect calculations. We show that $BaZrS_3$ is intrinsically n-type, and that p-type doping of

BaZrS$_3$ will be very difficult due to strong compensation by intrinsic donor defects. While BaZrS$_3$ shows high defect tolerance with few low formation energy, deep defects, the sulfur interstitial (S$_i$) is identified as the most worrisome nonradiative recombination center. Our results suggest pathways regarding growth condition optimization and device design towards high-performance BaZrS$_3$ absorbers.

Results

Electronic band structure and carrier transport

Figure 1. (a) Crystal structure of BaZrS$_3$. (b) HSE06-calculated electronic band structure and (partial) density of states (DOS) of BaZrS$_3$.

BaZrS$_3$ forms in an orthorhombic *Pnma* perovskite structure (see Figure 1a). Our calculated band structure using the Heyd-Scuseria-Ernzerhof hybrid functional (HSE06)[38] shows a direct band gap of 1.81 eV at the Γ point (Figure 1b), in agreement with previous calculations and experiment.[4,10,16–22,39] Combining computed electronic and phonon properties, we find a phonon-limited carrier mobility of 11 cm^2/Vs for holes and 37 cm^2/Vs for electrons, with the carrier scattering mechanism dominated by polar optical phonons (see the supporting information for details). These values are upper bounds as realistic polycrystalline

films will have additional scatterings from grain boundaries, impurities, and others. They are much lower than those calculated for conventional thin-film inorganic solar absorbers (such as CdTe[40,41] and Cu_2ZnSnS_4[42]). The calculated hole mobility of $BaZrS_3$ is also lower than for the halide perovskite $CH_3NH_3PbI_3$ (11 vs 47 cm^2/Vs), yet these two materials have comparable calculated electron mobility.[43] Our results are consistent with experiments on $BaZrS_3$ thin films which indicate low carrier mobilities ($\sim$2 cm^2/Vs for holes and $\sim$10–20 cm^2/Vs for electrons).[24,25,44,45] The measured low carrier mobility has been often attributed to small grain size or impurity scattering.[24,25] While these could be limiting factors in the experiments, our results highlight that $BaZrS_3$ has intrinsically low phonon-limited carrier mobility, and that experimentally it is very unlikely to achieve mobilities higher than our computed values. We note that Ye *et al.* reported a very high sum mobility ($>$100 cm^2/Vs) in $BaZrS_3$ films based on time-resolved photoluminescence (TRPL) measurements but the data suffer from reported very large uncertainty.[46]

The large difference between hole and electron mobilities directly comes from the electronic band structure (see Figure 1b). The lower conduction bands are much more dispersive than the upper valence bands. As a result, the effective mass is found to be small for electrons (0.3 m_0) and relatively large for holes (0.9 m_0). The fundamental difference in hole effective mass and mobility between $BaZrS_3$ and $CH_3NH_3PbI_3$ comes from the different electronic character in the valence band. While the halide perovskite mixes anion and cation orbitals leading to delocalized valence band,[47] the sulfide shows a more ionic behavior with the valence band being mainly of anion character (see Figure 1b).

Intrinsic point defects and doping

We have calculated all the intrinsic point defects in $BaZrS_3$ including the vacancies (V_{Ba}, V_{Zr}, V_S), interstitials (Ba_i, Zr_i, S_i), and antisites (Ba_{Zr}, Zr_{Ba}, Ba_S, S_{Ba}, Zr_S, S_{Zr}). Our first-principles calculations are all performed using the HSE06 hybrid functional and large $3\times3\times2$ supercell (360 atoms) with proper charge correction and spin-polarization, which is different

from previous first-principles calculations.[16,48] We provide in the supporting information the details of our methodology and a comparison to previous calculations. We note that some of the defects (e.g., S_i) involve several configurations that are close in energy. In the following, we report only results for the lowest energy configurations, while those for metastable configurations can be found in Figure S2 of the supporting information.

Figure 2. Formation energies of intrinsic point defects in $BaZrS_3$ as a functional of Fermi level, under (a) S-poor and (b) S-rich conditions. The Fermi level is referenced to the valence-band maximum (VBM) of $BaZrS_3$. The slopes of the formation-energy lines indicate defect charge states, and the dots denote charge-state transition levels (see also Figure 3).

Figures 2 shows the formation energies of the intrinsic defects in $BaZrS_3$ for both S-poor and S-rich conditions. The defect charge-state transition levels are plotted in Figure 3. We find that a series of shallow donor defects can form in $BaZrS_3$. The V_S is the dominant donor, giving rise to two donor levels $(+/0)$ and $(2+/+)$ that are almost in resonance with the conduction band. Under S-poor conditions (Figure 2a), the V_S has fairly low formation energy and thus exists in high concentration. On the other hand, the acceptor defects, mainly V_{Ba} and Ba_{Zr}, have high formation energies. These indicate that S-poor $BaZrS_3$ will be heavily n-type doped by the V_S donors. Under S-rich conditions (Figure 2b), the formation energy of V_S is increased, while the formation energies of the acceptor defects are reduced. Under those conditions, the equilibrium Fermi level would be pinned close to the intersection of the formation energies of V_S and V_{Zr} (about 0.5 eV below the conduction band), indicative of

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a very weak n-type, almost intrinsic $BaZrS_3$. Our results explain the experimental observation that as-grown $BaZrS_3$ is intrinsically n-type with the electron concentration as high as 10^{19}–10^{20} cm^{-3},[24] and we attribute this doping to sulfur vacancies.

Figure 2 also indicates that it will be very difficult to achieve p-type $BaZrS_3$. While V_{Ba}, V_{Zr}, and Ba_{Zr} are shallow acceptors, they are strongly compensated by the V_S donors. Even under the most favorable S-rich conditions, Fermi-level pinning energy for p-type doping[49,50] is 0.6 eV above the VBM, caused by the V_S whose formation energy drops first to zero when the Fermi level is approaching the VBM (Figure 2b). In view of the high p-type pinning limit, any extrinsic shallow acceptors will be strongly compensated, thus preventing p-type doping. In the literature, p-type $BaZrS_3$ has only been reported once with hole concentration of $\sim 10^{18}$ cm^{-3}.[27] We note that this was achieved in a sample which is extremely Ba-deficient (Ba/Zr ratio as low as ~ 0.6), raising questions about possible secondary phases.

Figure 3. Defect charge-state transition levels $\epsilon(q/q')$. Only the levels falling into the $BaZrS_3$ band gap are shown. The red and blue bars denote acceptor and donor levels, respectively.

Next to doping, from Figures 2 and 3 we identify a few defects with deep transition levels, including V_{Zr} (3−/4−), Ba_{Zr} (−/2−), S_{Ba} (+/3−), S_{Zr} (0/2−), and S_i (0/2+). Only S_i has sufficiently low formation energy to exist in significant concentration (when in S-rich

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conditions; see Table S4 for the calculated defect concentrations). Since defect-assisted non-radiative recombination is one of the key processes that limit carrier lifetime and ultimately solar cell performance,[51–57] it is necessary to assess whether the S_i is an efficient nonradiative recombination center.

Nonradiative carrier capture by sulfur interstitials

We now compute the nonradiative capture coefficients of the S_i. For nonradiative capture by the S_i, the relevant charge-state transitions are $(2+/+)$ and $(+/0)$, which are located at 0.35 and 1.37 eV above the VBM, respectively, as shown in Figure 4a. There are two capture processes associated with the $(+/0)$ level: C_p^0 for hole (p) capture and C_n^+ for electron (n) capture, where the superscript denotes the initial charge state.[58,59] Similarly, nonradiative recombination via the $(2+/+)$ level involves two capture processes: C_p^+ and C_n^{2+}.

To illustrate the capture processes, Figure 4b shows the local atomic structures of the S_i in the three charge states: 0, +, and 2+. The local structures of S_i^0 and S_i^+ are similar but differ from that of S_i^{2+}. In the 0 and +1 charge states, the interstitial S forms distorted tetrahedral bonds with two Ba, one Zr, and one S nearest neighbors. With the $S_i^0 \rightarrow S_i^+$ transition (i.e., capturing a hole, C_p^0), another lattice S atom moves towards the interstitial S. This lattice S atom and the interstitial S move further closer with the $S_i^+ \rightarrow S_i^{2+}$ transition (i.e., capturing another hole, C_p^+). As a result, the S_i^{2+} forms a S trimer.

The configuration coordinate diagrams (CCDs) for the S_i $(+/0)$ and $(2+/+)$ transitions are shown in Figures 4c and 4d. Such diagrams map the potential energy surfaces (PESs) of a defect in two adjacent charge states for a given transition as a function of a generalized configuration coordinate (Q).[60–62] We find that the Q displacement is larger for the $(2+/+)$ transition than for the $(+/0)$ transition, reflecting the structural differences discussed above. The CCDs indicate anharmonic atomic vibrations in the S_i capture processes, which are pronounced for those associated with the $(2+/+)$ transition; see a comparison between the anharmonic and harmonic PESs in Figures 4c, 4d and S3. Anharmonicity in the CCDs was

Figure 4. (a) Formation energy of the sulfur interstitial (S_i) versus Fermi level under S-rich conditions. (b) Local atomic structures of the S_i in the 0, +, and 2+ charge states. (c)–(d) Configuration coordinate diagrams for the S_i (0/+) and (+/2+) transitions. The intersection of the PESs indicates the capture barriers. The gray dashed lines are a harmonic fit of the PESs. (e) Temperature-dependent nonradiative capture coefficients of the S_i.

widely found for nonradiative carrier capture in halide perovskites and other low-symmetry semiconductors.[59,63–66] The anharmonicity reduces the electron capture barrier of S_i^{2+} but increases the electron capture barrier of S_i^+, compared to capture barriers in the harmonic approximation. Both S_i^0 and S_i^+ have a negligibly small hole capture barrier. From the capture barriers, the S_i is expected to be an efficient nonradiative recombination center.

Figure 4e shows the calculated four capture coefficients versus temperature. The results suggest fast electron capture by S_i^{2+} with C_n^{2+} of 6.6×10^{-6} cm^3/s at room temperature and slow electron capture by S_i^+ with C_n^+ of 1.95×10^{-10} cm^3/s. The hole capture by S_i^0 is fast with a room-temperature C_p^0 of 1.97×10^{-7} cm^3/s, while it is slow for S_i^+ with C_p^+ of 1.05×10^{-9} cm^3/s. The latter is due to relatively small vibrational overlap between the PESs for the $S_i^+ \rightarrow S_i^{2+}$ transition. In low-doped or intrinsic BaZrS$_3$, by balancing electron

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and hole capture under steady-state conditions, the total capture coefficient (C_{tot}) is given by[58,66]

$$C_{\mathrm{tot}} = \frac{C_n^+ + C_p^+}{1 + \frac{C_n^+}{C_p^0} + \frac{C_p^+}{C_n^{2+}}}.$$

At room temperature, the C_{tot} is calculated to be 1.25×10^{-9} cm^3/s. This is a moderate value, limited by the relatively slow hole and electron capture by S_i^+. It is slightly smaller than the value (7×10^{-9} cm^3/s) for the dominant recombination centers (iodine interstitials, I_i) in $CH_3NH_3PbI_3$ computed in a similar theoretical framework.[59,63]

Discussion

$BaZrS_3$ shows higher electron mobility than hole mobility which would suggest using this material as a p-type absorber layer as it is the diffusion length of minority carriers that mainly controls the solar cell efficiency.[67,68] Our analysis however shows that it will be unlikely to make p-type $BaZrS_3$. Using the intrinsically n-type doped $BaZrS_3$ as an absorber layer will lead to smaller minority-carrier diffusion lengths limited by the lower hole mobility and also cause issues at the device level as discussed for other n-type absorbers.[69,70] We thus suggest it could be more viable to devise a p-i-n (or n-i-p) cell using $BaZrS_3$ as the intrinsic layer (lightly n-type doped), as in halide perovskite solar cells.[71] In such a p-i-n device, the carrier diffusion length is controlled by the ambipolar mobility (μ_{a}) which is estimated to be 17 cm^2/Vs using our calculated intrinsic electron and hole mobilities.[72–74] Preparing intrinsic $BaZrS_3$ requires to reduce dramatically the concentration of V_S donors which can be achieved using S-rich growth conditions. However, S-rich conditions would enhance the formation of the nonradiative recombination centers, the S_i. It might then be beneficial to reduce electron concentration by introducing an extrinsic shallow acceptor while keeping a low sulfur chemical potential.

We estimate now a realistic upper bound of the S_i density in high-temperature synthesized $BaZrS_3$ samples. Under S-rich conditions and assuming 1000 K growth of $BaZrS_3$ and rapid

quenching to room temperature, the S_i density is estimated to be on the order of 10^{17} cm^{-3} (see Table S4). This high S_i density leads to a nonradiative recombination coefficient (A) on the order of 10^8 s^{-1} at room temperature; here A is defined as $A = N_d C_{tot}$, where N_d is the defect density.[59,75,76] As a result, the nonradiative lifetime ($\tau = 1/A$) is on the order of 10 ns for S-rich conditions. Moving to less S-rich conditions will reduce the S_i density and increase the carrier lifetime. Our results are in reasonable quantitative agreement with the carrier lifetime on the order of 50 ns measured by TRPL on BaZrS$_3$ single-crystal samples.[46] In comparison, the I_i in CH$_3$NH$_3$PbI$_3$ has been found to lead to a much longer nonradiative lifetime, on the order of 100 ns,[59,63] based on the fact that the deep-level trap density in solution-processed CH$_3$NH$_3$PbI$_3$ samples is on the order of 10^{15} cm^{-3}.[77–79]

Ye *et al.* estimated the solar cell figure of merit (F_{PV}) of BaZrS$_3$ based on experimental data and using $F_{PV} = \alpha * L_D$, where α is the optical absorption coefficient and $L_D = \sqrt{\frac{\mu_a k_B T}{e} \tau}$ the carrier diffusion length.[46,72,80–82] They found a F_{PV} value of 2.1 using an absorption coefficient of 4940 cm^{-1}, nonradiative lifetime of 50 ns, and mobility of 146.2 cm^2/Vs.[46] Our computational results do not disagree with the lifetime but raise strong doubts on the mobility value. Since our calculated mobility is an order of magnitude lower, we estimate the F_{PV} to be 0.33. Our results however indicate that if the S_i concentration is lowered or the interstitials are passivated in some way, higher carrier lifetime could be reached which will boost the figure of merit.

In addition to intrinsic defects, we briefly mention that BaZrS$_3$ is tolerant to oxygen impurities which could be present in high concentration in the samples prepared by sulfurization of BaZrO$_3$ precursor.[24,83] We find that the oxygen-related point defects, including oxygen interstitial (O_i) and O substitution on the S site (O_S), are electrically inactive, i.e., they are stable in the neutral charge state for almost the entire range of Fermi levels (see Figure S4 of the supporting information), in agreement with previous experimental and theoretical studies.[83]

Conclusions

We evaluated carrier transport and defect properties in the chalcogenide perovskite solar absorber $BaZrS_3$. Our results show that $BaZrS_3$ has a lower hole mobility than electron mobility (11 vs 37 cm^2/Vs). The mobility in this sulfide perovskite is lower and more asymmetric (in terms of hole versus electron mobilities) than in lead halide perovskites. Our defect computations indicate an intrinsic tendency for n-type doping due to the shallow donor V_S and that p-type doping is very unlikely to be achievable. We confirm that overall $BaZrS_3$ is a defect-tolerant absorber with few deep defects that could act as nonradiative recombination centers. The S_i is identified to be the most problematic deep center. Under S-rich conditions, the carrier capture by the S_i will lead to a carrier lifetime on the order of 10 ns. Our work strongly suggests that suppressing the formation of S_i is critical for $BaZrS_3$ to be a high-performance absorber.

Supporting Information Available

Full description of the computational methods. Supplementary Tables S1–S5, Figures S1–S4, and Refs. S1–S29.

Notes

The authors declare no competing financial interest.

Acknowledgments

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