Importance of Many-Body Dispersion in the Stability of Vacancies and Antisites in Free-Standing Monolayer of MoS$_2$ from First-Principles Approaches

Arunima Singh,* Pooja Basera, Shikha Saini, Manish Kumar, and Saswata Bhattacharya*©

Department of Physics, Indian Institute of Technology Delhi, New Delhi 110016, India

Supporting Information

ABSTRACT: Defects in MoS$_2$ monolayer play a vital role in altering the electric and optical properties, which is a crucial factor in various semiconductor and optoelectronic devices. In the present work, we have investigated the thermodynamic stability of point defects in MoS$_2$ monolayer by means of first-principles-based density functional theory (DFT) and $ab$ initio atomistic thermodynamics. We have considered three vacancies and five antisites in our system, viz., Mo vacancy (V$_{Mo}$), S$_{Mo}$ antisite, S$_{2Mo}$ antisite, S vacancy (V$_S$), MoS antisite, S$_2$ vacancy (V$_{S2}$), Mo$_{S2}$ antisite, and 2Mo$_{S2}$ antisite. Our approach includes (i) the two-body van der Waals interaction under Tkatchenko–Scheffler scheme and (ii) many-body dispersion to account the effect of polarization on the defects’ stability. The many-body dispersion has posed a significant change in the pattern of stable defects. Hence, we report the stable defect states as observed by hybrid DFT with many-body dispersion as $V_{S^{-2}}, V_{Mo}$, and $S_{Mo}$ in n-type MoS$_2$ monolayer and $V_{S}^{-2}, V_{Mo}$, and $S_{2Mo}$ in p-type MoS$_2$ monolayer. Among these stable defect states, $S_{Mo}$ and $S_{2Mo}$ states have tuned the band gap of MoS$_2$ monolayer in the range of 1.1–1.8 eV. Therefore, their optical response in comparison to pristine has inferred their applicability in photovoltaics. Finally, we obtain that these defects have significant concentration in the finite temperature range of 50–1000 K. Our results, therefore, predict the p-type defect states in MoS$_2$ monolayer that would be helpful in device fabrications.

INTRODUCTION

Transition metal dichalcogenides (TMDs) constitute a field of high research interest due to their unique properties. These are the layered materials with interlayer van der Waals (vdW) forces and intralayer covalent bond. They exhibit indirect to direct band gap transition, as the dimension is reduced from bulk to monolayer. Molybdenum disulfide (MoS$_2$) is the most studied TMD material, owing to its abundance and low cost. Monolayer of MoS$_2$ features exceptional optical, electrical, and mechanical properties. It has a tunable band gap, and therefore, its electronic and optoelectronic properties can be controlled as per different requirements. Hence, MoS$_2$ is a promising material for future applications in device engineering, optoelectronics, and sensors.

Monolayers are manufactured by various experimental state-of-the-art methods, viz., chemical vapor deposition (CVD), sulfurization, chemical and mechanical exfoliation techniques, etc. Similar to any other material, defects are inadvertently introduced during its manufacture. These imperfections affect the mechanical, electrical, electronic, optical, and magnetic properties of the system. For instance, the electrical conductivity is largely affected as the defect constrains the mobility. The defects create different impact on the material of reduced dimensions than that on its bulk counterpart. These issues have been the focus of many experimental and theoretical studies. Characteristic of the defects under a given condition is a matter of understanding on the basis of which we may want to eliminate or induce a defect. Since defects alter the properties of the materials, these can be engineered for diverse applications. Defect engineering has its utilization in the field of spintronics, catalysis, electrochemical reactions, and semiconductors.

Among many characteristics pertaining to this system, the often observed n-type doping of MoS$_2$ has also been the motivation for conducting defect studies on the material. The stated observation is usually attributed to the large amount of native S vacancies. However, one needs to consider both n-type and p-type monolayers of MoS$_2$ for any requisite device application. Hence, the defect states that affect the thermodynamic stability of p-type monolayer are essential to be discussed. In addition, the van der Waals interactions affect the stability and mobility of the point defects in the semiconductors. The polarization which results in van der Waals interactions might affect the defect states leading to a change in the free energy of formation and, hence, in the stability. The field of defect studies on the TMD monolayers, though significantly studied, has not established a complete database.

In this article, we therefore intend to analyze the thermodynamic stability of native point defects using density functional theory (DFT) and $ab$ initio atomistic thermodynamics to evaluate the effect of polarization on the stable defect states in MoS$_2$ monolayer.
functional theory (DFT). First, we have validated the exchange-correlation functionals, viz., LDA, PBE, and HSE06 for the MoS$_2$ monolayer. Subsequently, to determine the most stable defect states, with the ground state defect configurations we have calculated the formation energies of the neutral and charged defects. We have modeled eight possible defect configurations, which consist of three vacancies and five antisites. Here, Mo, S, and S$_2$ vacancies and S$_{Mo}$, S$_{Mo}$, Mo$_{S}$, Mo$_{S}$, and 2Mo$_S$ antisites are shown in Figure 1. Following

![Figure 1](image_url)

**Figure 1.** Optimized geometries of the defects within the MoS$_2$ monolayer.

In this, in the expression of defect’s formation energy, we have included the dispersion corrections as per (i) the two-body van der Waals interaction using the Tkatchenko–Scheffler scheme (TS)$^{46}$ and (ii) many-body dispersion (MBD).$^{47,48}$ We have also shown results without including vdW effects just as a reference. The concentration of these defect states in the temperature range of 50–100 K using ab initio atomistic thermodynamics approach$^{49−51}$ has established the most important defects in doped MoS$_2$ monolayer. Further, we have obtained the optical response of those stable defect states which have tuned the band gap that includes the visible region of the spectrum.

### METHODOLOGY

We have employed first-principles-based methodology under the framework of density functional theory (DFT).$^{52−55}$ The calculations are performed with all-electron-based code DFT which uses numeric, atom-centered basis set.$^{56−59}$ We have presented here an exhaustive scenario on the choice of exchange correlation functionals starting from local/semilocal functional to more advanced hybrid functional especially to capture the effect due to exact exchange.$^{60,61}$ The respective functionals that we have employed here are proposed by Perdew–Burke–Ernzerhof (PBE)$^{62}$ and Heyd–Scuseria–Ernzerhof (HSE06).$^{63}$ The hybrid functional (HSE06) considers 25% mixing ($\alpha$) of the short-range Hartree–Fock exchange. Its long-range part is described by GGA-PBE functional. The screening parameter ($\omega$) of 0.21 bohr$^{-1}$ is optimized for the calculations. The following equation defines the exchange correlation energy for this functional.

$$E_{xc}^{HSE06} = \alpha E_{xc}^{HF,SR}(\omega) + (1 - \alpha) E_{xc}^{PBE,SR}(\omega) + E_{xc}^{PBE,LR}(\omega) + E_{xc}^{PBE}$$

In the bulk form, MoS$_2$ has trigonal prismatic structure.$^{64}$ A $6 \times 6 \times 1$ supercell of MoS$_2$ monolayer, consisting of 108 atoms, has been modeled. This size of the supercell keeps increasing until it aptly localizes the defects. In the calculations, the Brillouin zone was sampled by $4 \times 4 \times 1$ k-grid. Tier-2 basis sets for atoms with “tight” settings have been applied.$^{65}$

Note that, in order to avoid any artifact due to choice of DFT functionals, we have validated first the DFT functionals by calculating the 2D modulus of elasticity and compared it with the available experiments from the literature. The validation has been performed for the three functionals, viz., LDA, PBE, and HSE06. The total energy vs lattice parameter plot is obtained, and the modulus of elasticity is calculated at the minimum energy point (see Figure S1 in the Supporting Information for details). We have obtained the values as 159, 161, and 173 N/m, respectively, for the MoS$_2$ monolayer from LDA, PBE, and HSE06 functionals. Our results from HSE06 functional are in close agreement with the experimental value (170 N/m) of the elastic modulus.$^{65}$ Moreover, since the values obtained from LDA and PBE are comparatively close, we have presented here the results obtained from PBE and HSE06 functionals for the rest of the study. This comparative study of the functionals has been undertaken to ensure the importance of hybrid functionals and the possible error one may come across from employing local/semilocal functionals. Note that the two-body vdW interaction (TS scheme)$^{66}$ and many-body dispersion scheme$^{47,48}$ are being thoroughly benchmarked on both the PBE and HSE06 functionals. The correction parameter is based on Hirshfield partitioning of the electron density.

The absorption spectra have been obtained by HSE06 functional under the Vienna ab initio simulation package (VASP)$^{66}$ that implements PAW pseudopotential method.$^{57}$ Conjugate gradient minimization has been employed with 2 × 2 × 1 K-mesh for optimizing the force in the structures up to 0.001 eV/Å. The energy calculations for the structure have been performed with Brillouin zone sampling of 6 × 6 × 1 gamma-centered K-mesh with 0.01 meV energy tolerance. The plane wave energy cutoff is set to 500 eV for ground state calculations. The imaginary part of the obtained dielectric function gives the optical absorption of the system.

### RESULTS AND DISCUSSIONS

#### Stability in Defect States

The free energy of formation of charged defects can be calculated with the help of the following expression:

$$E_i = F_i^{(q)} - F_i^{(0)} + \sum_i N_i \mu_i + q_i (\mu_e + \Delta V + VBM)$$

Here, $E_i$ is the free energy of formation of the defect state. $F$ is the Helmholtz free energy, which is sum of total DFT energy and vibrational energy due to lattice vibration. Since the contribution of the latter term is not much and we are taking differences of $F_i^{(q)}$ and $F_i^{(0)}$ the effect due to lattice vibration will be insignificant. Therefore, the dominating term in $F$ is total DFT energy. Hence, it is important to compute it accurately after thorough validation of DFT functionals. $\mu_i$ is the chemical potential of the component $i$, $N_i$ is the number of vacancies or antisites, $\mu_e$ is the chemical potential of an electron, $\Delta V$ is the difference between core levels of pristine and defected supercell, and VBM denotes valence band maximum of the pristine neutral. The charge transition levels are given with respect to this VBM, and $\mu_e$ is varied within the band gap (see discussion for charged defects later). However,
in the case of neutral defects \((q = 0)\), the free energy of formation reduces to the following expression:

\[
E_f = E_{\text{defect}}^{(0)} - E_{\text{pristine}}^{(0)} + \sum N \mu_i
\]  

(3)

MoS\(_2\) layers act as a thermodynamic reservoir thereby making the chemical potentials of Mo and S interdependent.\(^{68}\) Hence, we have

\[
\Delta H_f(\text{MoS}_2) = \mu_{\text{MoS}} - (\mu_{\text{Mo}} + 2\mu_S)
\]  

(4)

where \(\Delta H_f(\text{MoS}_2)\) is the formation enthalpy, i.e., 2.44 eV at 300 K for this system.\(^{69,70}\) In equilibrium with the MoS\(_2\) bulk, \(\mu_{\text{Mo}}\) and \(\mu_S\) are related through the following expression:

\[
\mu_{\text{Mo}} + 2\mu_S = E_{\text{MoS}}
\]  

(5)

The chemical potentials can never exceed the value of the corresponding condensed pure element.\(^{52}\) Therefore, we have physical permissible limits as \(\mu_{\text{Mo}} \leq E_{\text{Mo}}\) (Mo-rich limit) and \(\mu_S \leq E_S\) (S-rich limit). The Mo-rich limit can also be termed as S-poor limit with expression \(\mu_{\text{Mo}}^{\text{min}} = (E_{\text{MoS}} - E_{\text{Mo}})/2\). The corresponding values are found from the formation enthalpy of MoS\(_2\). Hence, we obtain the limiting conditions for the chemical potential of S \((\mu_S)\) as \(-1.22 \leq \Delta \mu_S = \mu_S - E_S \leq 0\).

In equilibrium, the negative values of free energy of formation correspond to the stable defect configurations with respect to the pristine monolayer. Under this consideration, we observe that neutral defect states are more stable than the pristine monolayer (see Figure S2 in the Supporting Information). However, as previously discussed, defects are inevitable in the material, which further indicates the presence of extra charge in the system. Note that the formation energy of one isolated defect can be reduced significantly by several electronvolts when the charge carriers (holes or electrons) are available in the material.\(^{49}\) Therefore, we have analyzed the defects with \(-2, -1, +1, \) and \(+2\) charged states by the two functionals (PBE and HSE06). We now analyze the variation of free energy of formation of the defect as a function of chemical potential of electron \((\Delta \mu_e)\) within S-rich \((\Delta \mu_S = 0)\) and Mo-rich \((\Delta \mu_S = -1.22)\) limits. Figure 2a and Figure 2b correspond to the plots obtained by HSE06 functional for S vacancy defect states. The plots corresponding to other defect states and PBE functional have been provided in the Supporting Information. Here, we observe that \(V_{S^2}\) and \(V_{Mo^2}\) are the most stable defect configurations near CBm (conduction band minimum) and VBM, respectively. However, these states appear to be more stable than pristine, only in the Mo-rich condition. Similar plots have been obtained for other defect configurations as well, where the plot corresponding to the Mo antisite inferred them to be highly improbable (see Figures S3–S8 in the Supporting Information).

Note that these plots give an idea about the stability of certain defect states for others but only at a fixed \(\Delta \mu_S\) condition (viz., here plotted at S-rich and Mo-rich limiting conditions). In order to gain more clarity, we have considered a 3D phase diagram (see Figure 2c), where along the \(x, y, \) and \(z\)-axes we have respectively plotted \(\Delta \mu_S\) and \(E_f\). The \(x-y\)-plane is being viewed here from the negative \(z\)-axis (the lower the \(E_f\), the more stable the configuration). From Figure 2c the most stable defect configurations among the neutral and all possible charged defects are determined (as obtained from the HSE06 functional). Each color in the phase diagram is associated with a defect configuration, and the region of a specific color represents the range of \(\Delta \mu_S\) and \(\Delta \mu_e\) where the corresponding configuration is stable. This plot covers the full range of chemical potential of sulfur, i.e., \(-1.22 \leq \Delta \mu_S \leq 0\), and chemical potential of electron, i.e., \(0 \leq \Delta \mu_e \leq 1.8\). Moreover, the phase diagram also considers the positive values of free energy of formation of defects, which might be probable in real situations. At the Mo-rich condition, we have observed \(V_{S^2}\) and \(V_{Mo^2}\) as the most stable states near CBm and VBM, respectively. This is in agreement with the observation from Figure 2a and Figure 2b.

This phase diagram helps to infer whether the stable defect states are acceptors or donors depending on the position of stability over the bandgap. If a defect accepts an electron to gain stability, it will have negative charge associated with it and hence will act as an electron acceptor. Similarly, positively-charged defects have lost electrons to gain stability and hence act as electron donors. Moreover, when \(\Delta \mu_e\) is near to CBm this situation can be stated as n-type MoS\(_2\) monolayer. Similarly, \(\Delta \mu_e\) nearer to VBM is the situation of p-type MoS\(_2\) monolayer. In the phase diagrams, negative defect states are stable near CBm, and positive defect states are stable near VBM, hence inferring their stability in n-type and p-type monolayer, respectively.

**Effect of van der Waals Interactions in the Stability.**

The vdW interaction originates as a result of polarization in the material. It is a part of long-range nonlocal correlation energy. The polarization refers to the induced dipole in the system, which will definitely affect the defect states and the charge associated with it. Hence, we have obtained the 3D phase diagrams (Figure 3) for the most stable defect configurations, under two-body vdW interaction and many-body dispersion, with PBE and HSE06 functionals. We have observed the same defect states as the most stable configurations, by PBE and HSE06 functional under two-body vdW interaction (i.e., PBE +TS (Figure 3a) and HSE06+TS (Figure 3b)). The n-type and p-type MoS\(_2\) monolayers have \(V_{S^2}\), \(V_{Mo^2}\), \(S_{Mo^2}\) and \(V_{S^2}\), \(S_{Mo^2}\) as the most stable states, respectively.

Further, on analyzing the phase diagrams under many-body dispersion (Figure 3c and Figure 3d), we see considerable change in the stability pattern of the defect states. The phase
diagram obtained by the HSE06 functional (Figure 3d) shows the emergence of the new defect states of $V_{Mo}^{2-}$ and $S_{Mo}^{2-}$ in the S-rich limit for the case of p-type MoS$_2$ monolayer. Moreover, the $V_{Mo}^{2-}$ state is absent from the phase diagram obtained by the PBE functional (Figure 3c) for the case of n-type MoS$_2$ monolayer. The HSE06 functional incorporates the Hartree–Fock exchange term, which is not the case in the PBE functional. Therefore, electron localization is more accurate in the case of HSE06, we report here the inference corresponding to HSE06 functional with many-body dispersion (HSE06+MBD) correction.

We now intend to get insight into the energetics of the two functionals under the situations of no vdW interaction, TS, and MBD. Hence, by visualizing the 2D phase diagram in Figure 4 at S-rich limit, we see that mostly $S_2Mo^{+2}$ and $V_{Mo}^{2-}$ have very close values of free energy of formation, making these likely to occur in monolayer. The corresponding phase diagram of HSE06+MBD is an exception, where $S_{Mo}^{2-}$ has comparatively high free energy of formation (i.e., less stable). Hence, on observing all the phase diagrams, we understand that there is definitely some competition in free energy of formation of few defects, and in a real experiment all of them should have finite probability to occur simultaneously. It is therefore even more interesting to understand the concentration of such defects with varying temperatures.

**Defect Concentration.** After the observation of varied range of stable defects, it becomes imperative to compute the concentration of defects at higher temperatures in order to understand the defect stability. The effect of environment is incorporated using *ab initio* atomistic thermodynamics.$^{50}$

![Figure 3. 3D phase diagrams that show most stable defect states by the PBE and HSE06 functionals under the two-body vdW interaction (TS) and many-body dispersion (MBD).](image)

![Figure 4. Variation of free energy of formation of defect states observed at S-rich limit in 3D phase diagrams by PBE (upper panel) and HSE06 (lower panel) functionals under the two-body vdW interaction (TS) and many-body dispersion (MBD).](image)

The equation for the chemical potential of sulfur ($\mu_S(T, p) = \frac{1}{2} \mu_{S^2}(T, p_S)$) can be written as follows:

$$\mu_S(T, p_S) = -k_BT \ln \left( \frac{2m}{\hbar^2} \right)^{3/2} \left( k_BT \right)^{3/2} + k_BT \ln p_S$$

$$- k_BT \ln \left( \frac{8\pi^2 k_BT}{\hbar^2} \right) + k_BT \ln \left[ 1 - \exp \left( \frac{\mu_S}{k_BT}\right) \right]$$

$$- k_BT \ln M + k_BT \ln \sigma$$

where $m$ is the mass, $M$ is the spin multiplicity, and $\sigma$ is the symmetry number. The above expression includes translational, rotational, vibrational, spin, and symmetry degrees of freedom for gaseous molecule of $S_2$. We have considered two conditions for chemical potential of electrons, i.e., $\Delta \mu_e = 0$ eV at VBM and $\Delta \mu_e = 1.8$ eV at CBm, for calculating the concentration of defects under different functional energetics.

If $N$ is the total number of atomic sites in the lattice and $E_{fi}$, the free energy of formation of any one kind of defect (let it specify as type-$n$), then the number of type-$n$ defect states, $N_n$, is given as

$$N_n = \frac{N - \sum_{m\neq n} N_m}{1 + \exp(\beta E_{fi})}$$

where $N_n$ is the number of the defect states (specified as type-$m$) other than type-$n$ and $\beta = 1/k_BT$. An equation similar as above can be written for each defect type, and their solution will provide the concentration at a finite temperature.$^{59,71}$

$$\frac{N_n^e}{N} = \frac{\exp(-\beta E_{fi})}{1 + \sum_{m\neq n} \exp(-\beta E_{fi})}$$

We have computed eq 8 for analyzing the concentration of defect states at the finite temperatures. The plot gives the variation of logarithmic percentage concentration of various defects as a function of temperature. The 100% concentration of a defect in the system corresponds to the value of logarithmic percentage concentration as 2. The partial pressure $p_S$ is fixed at 1 atm, and $\Delta \mu_s$ is set at VBM and CBm.
The concentration plots are obtained for PBE and HSE06 functional under the consideration of TS (Figure 5) and MBD (Figure 6). The earlier discussions stated that positive charges are stable near VBM and negative charges are stable near CBm, and the same is evident from the concentration plots as well. Figure 5 is in correspondence with the 3D phase diagrams of PBE+TS (Figure 3a) and HSE06+TS (Figure 3b). The most stable defect configurations have significant concentrations at the finite temperatures and are accompanied by the concentrations of other defect states, viz., VS+1, VS−1, VS2+2, and VS2−2. These concentration plots will help in indicating the occurrence of the defect states, when the monolayer is exposed to the corresponding environmental conditions.

We observe from the Figure 6 that the SMo−2, V−2, and V−2Mo achieve significant concentration in the n-type monolayer. The 3D phase diagram for the case of PBE+MBD (Figure 3c) does not display V−2Mo as most stable state; however, it achieves a significant concentration comparable to that of SMo2 and VS−2. Hence, unanimously we observe that the stable defect states which have significant probability at finite temperatures for n-type monolayer are SMo2, VS−2, and V−2Mo. In the p-type case, we see +2 charged state of the defects as stable. The stability of +2 and −2 charged states can be possibly attributed to the electronic configuration of the S (3s23p4) and Mo (4d55s1). They both have six valence electrons; therefore, the antisite (SMo) and the vacancies (VS and VMo) can be both donor and acceptor at VBM and CBm, respectively. However, S vacancies are observed to be the abundant defects. These could be created with S2− ions leaving the site, and hence, as per charge neutrality, S vacancy would be stable at −2 charged state. It is clear from the phase diagrams and concentration plots that Mo vacancy is stable for a short range of ΔμS. This may be attributed to larger atomic radius and greater atomic mass of Mo than that of S.

The general trend of the defect states in n-type monolayer is in sync with the existing literature. The improbability of Mo antisites has also been inferred in the works of Hong et al. However, the obtained stable charged state differs from that of the previous works. The corresponding explanation has been attributed to the valence electronic configuration of the Mo and S atoms. Moreover, the S2Mo2−2 defect state is visible as the stable state in phase diagram with HSE06+MBD. The S2Mo phase has been discussed in the experiment and theoretical work of Zhou et al. Hence, this also gives an indication that HSE06+MBD correlates well with the experimental finding.

The aspect of defect states in p-type MoS2 monolayer and inclusion of many-body dispersion add to the broader defect literature of MoS2 monolayer. Further, the wide applicability of our inference is ascertained by obtaining the optical response of the defect states in comparison with the pristine, as discussed in the following section.

**Absorption Spectra.** Table S2 contains the information about the band gaps corresponding to stable defect states as obtained by HSE06 functional. We observe that SMo2 and S2Mo2 have band gap in the range 1.1−1.8 eV, which implies its application in photovoltaics. We have commented on its applicability by obtaining the absorption spectra (Figure 7) by HSE06 functional. The imaginary part of the frequency-dependent complex dielectric function, ε(ω) = Re(ε) + Im(ε), gives the absorption. The real part is calculated by the Kramers–Kronig relation. The basic contribution to the analysis of optical properties is achieved by the interband transitions.
and VS to the partial charges that occupy the orbitals. The optical response of S Mo showed significant enhancement in the visible region. Hence, in case these defect states are created or induced in the system, it may be utilized in the aforementioned applications. A small bump seen at 0.6 eV in the spectra corresponding to $S_{\text{Mo}}^{-2}$ is attributed to the partial charges that occupy the orbitals.

## CONCLUSIONS

An exhaustive study has been undertaken for understanding the stability of defect configurations in MoS$_2$ monolayer. We have observed that defect configurations are not stable in the neutral state and the Mo antisites are improbable to occur due to their high formation energies. The results have indicated that the stability of defect configurations depends on the many-body dispersion, and therefore, for accurate experimental correlation this should be incorporated in the studies. The most probable defect configurations as obtained by the HSE06+MBD are $V^+_5$, $V^+_6$, and $S_{\text{Mo}}^{-2}$ for n-type monolayer and $V^+_5$, $V^+_6$, and $S_{\text{Mo}}^{-2}$ for p-type monolayer. The $S_{\text{Mo}}^{-2}$ that appeared to be stable by HSE06 functional with MBD also showed significant concentration by HSE06 functional with the TS scheme of vdW. Further, the computed concentration of all the stable defect states verifies their presence at finite temperatures. In addition, we have observed red shift in the optical response of $S_{\text{Mo}}^{-2}$ and $S_{\text{Mo}}^{-2}$ from that of pristine, extending their applicability in photovoltaics. Since a defect-free MoS$_2$ monolayer is practically impossible, harnessing these defect states for absorption in photovoltaics is considerable. Moreover, there is enough scope of experimental understanding of the discussed point defects in p-type MoS$_2$ monolayer, which would pose an important inference for applications in device industry.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.9b09396.

(1) Validation of functional; (II) Free energy of formation of neutral antisites and vacancies; (III) Free energy of formation of charged states of antisites and vacancies; (IV) 3D phase diagrams of the most stable defect states without vdW interaction; (V) Band gap of the stable defect states (PDF)

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## REFERENCES


[Figure 7. Imaginary part of dielectric function (absorption spectra) as obtained by HSE06 functional.](https://pubs.acs.org/doi/10.1021/acs.jpcc.9b09396)


