Intrinsic defect properties in halide double perovskites for optoelectronic applications

Tianshu Li,¹ Xingang Zhao,¹ Dongwen Yang,¹ Mao-Hua Du,²* and Lijun Zhang¹,*

¹State Key Laboratory of Superhard Materials, Key Laboratory of Automobile Materials of MOE, and College of Materials Science and Engineering, Jilin University, Changchun 130012, China.
²Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States.

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Lead-free halide double perovskites with the formula of quaternary A’B’B”X₆ have recently attracted intense interest as alternatives to lead-halide-perovskite-based optoelectronic materials for their non-toxicity and enhanced chemical and thermodynamic stability. However, the understanding of intrinsic defect properties and their effects on carrier transport and Fermi level tuning is still limited. In this paper, we show that, by exploring the phase diagram of a halide double perovskite, one can control the effects of intrinsic defects on carrier trapping and Fermi level pinning. We reveal the ideal growth conditions to grow p-type Cs₂AgInCl₆ and Cs₂AgBiCl₆ as well as semi-insulating Cs₂AgBiBr₆ with low trap density for targeted photovoltaic or visible-light/radiation detection application.

Lead (Pb) halide perovskites have been extensively investigated for diverse applications, including photovoltaics [1-10], light-emitting diode [11-13], laser [14-16], and radiation detection [17-20], owing to their unique electronic and optical properties. However, the toxicity of Pb and the intrinsic material instability have hindered their development. Recently, inorganic Pb-free halide double perovskites (HDPs), which are a large class of quaternary compounds with a general formula of A’B’B”X₆, have attracted great attention as alternatives to Pb halide perovskites [21-31]. In particular, Cs₂AgInCl₆ and Cs₂AgBiX₆ (X=Cl, Br), which have been successfully synthesized in experiment and have the bandgap values of 2.0-3.0 eV and good material stability, have shown great potential as useful optoelectronic materials such as photovoltaic (PV) absorbers [32-35], photon and ionizing radiation detectors [36,37]. Cs₂AgInCl₆ exhibits direct band gap (2.0 eV according to the photoluminescence measure) as well as an ultra-long carrier lifetime (6 μs) [21,38-40], which are suitable for PV applications. However, Meng et al. reported that the optical absorption at the visible range in Cs₂AgInCl₆ may be significantly reduced due to the parity-forbidden transition at band edges [41]. Nevertheless, the low trap density (towards 10⁸ cm⁻³) in single-crystal Cs₂AgInCl₆ makes it a promising ultraviolet detector material [37], which may find applications in fire and missile flame detection as well as optical communications. Cs₂AgInBr₆, with a theoretically predicted direct band gap of ~1.50 eV [21], is expected to be a good PV absorber or visible-light detector, although its synthesis is still a challenge. In contrast to the direct band gaps found in Cs₂AgInX₆, Cs₂AgBiCl₆ and Cs₂AgBiBr₆ have indirect band gaps of 2.77 and 2.19 eV, respectively [25,29,42]. Despite their relatively large band gaps for PV applications, it has been reported that the solar cells based on Cs₂AgBiBr₆ films show power conversion efficiencies up to 2.5% without device optimization [43]. The efficiency might be further improved by narrowing the bandgap of Cs₂AgBiBr₆ via trivalent metal doping/alloying [31,44]. Moreover, the indirect band gap is desirable for a semiconductor photon/radiation detection material because a direct band gap would increase the rate of radiative recombination of the radiation-generated electrons and holes, which should be collected by electrodes. The heavy constituent atoms and the sufficiently large band gap renders Cs₂AgBiBr₆ a potential X-/gamma-ray detector material. Indeed, a recent experimental work demonstrated promising figure of merits of Cs₂AgBiBr₆ for X-ray detection [36].

To advance the development of Pb-free HDPs as PV or photon/radiation detection materials, comprehensive understanding of intrinsic defect properties is of vital importance because defects strongly affect carrier density and transport. Efficient carrier transport is critically important in both PV and photon/radiation detection applications. High resistivity is required for semiconductor photon/radiation detection materials whereas good n- or p-type conductivity is usually needed in PV materials. Therefore, the understanding of
carrier trapping at defects and carrier compensation is important for the development of HDPs for these optoelectronic applications. In this work, using advanced first-principle calculations, we identify deep defect levels that are detrimental to carrier transport in Cs$_2$AgInCl$_6$, Cs$_2$AgBiCl$_6$, and Cs$_2$AgBiBr$_6$, and show that chemical potentials of the constituent elements (which are associated with experimental growth conditions) can be modified to suppress unwanted deep level defects and to tune Fermi level for PV or photon/radiation detection applications.

We performed first-principles calculations based on density-functional theory, as implemented in the Vienna ab initio simulation package codes [45]. The electron-core interaction was described using the frozen-core projected augmented wave pseudopotentials [45,46]. The kinetic energy cutoff of 400 eV was used in all calculations. The lattice parameters and atomic positions were optimized using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [47]. The band gaps and the defect formation energies were further calculated using the screened Heyd-Scuseria-Ernzerhof (HSE) hybrid density functional [48,49] with the spin-orbital coupling (SOC) based on the PBE-optimized structures without further relaxation. The primitive cell and a 4x4x4 k-point mesh were used for obtaining the lattice parameters and band gaps while an 80-atom supercell was used for defect calculations. A 2x2x2 and a Γ-point-only k-point mesh were used for the PBE and HSE supercell calculations, respectively. The mixing parameters of 25%, 28% and 30% for Cs$_2$AgInCl$_6$, Cs$_2$AgBiCl$_6$ and Cs$_2$AgBiBr$_6$ were used in HSE calculations for more accurate description of electronic structures. The calculated lattice parameters and band gaps of Cs$_2$AgInCl$_6$, Cs$_2$AgBiCl$_6$ and Cs$_2$AgBiBr$_6$ agree well with the experimental results (see TABLE S1, Supplemental Material [50]). The calculations of defect formation energies and transition levels were performed with the standard supercell approach, as described in detail in Supplemental Material [50].

The crystal structure of a HDP is shown in FIG. 1a. The BX$_6$ and B'X$_6$ octahedra alternate along the three crystallographic axes such that the B and B' ions form a rock-salt-type ordering. The band structures and the density of states of Cs$_2$AgInCl$_6$, Cs$_2$AgBiCl$_6$, and Cs$_2$AgBiBr$_6$ are shown in FIGs. 1(b)-(c) and 5(a). Cs$_2$AgInCl$_6$ exhibits a direct band gap at the Γ point; the conduction band is derived from the In-5s states while the valence band states are mainly made up of Ag-4d and the Cl-3p states. In contrast, Cs$_2$AgBiCl$_6$, and Cs$_2$AgBiBr$_6$ have indirect band gaps; the conduction band minimum (CBM) is located at the Γ point while the VBM is at the X point. The Bi-6p states dominate the conduction band. For the valence band, in addition to the contribution from the Ag-4d and the halogen-p states, the fully-occupied Bi 6s states also hybridize with the valence band states. The coupling between the Bi-6s states and the directional Ag-4d states along the (100) direction moves the VBM from the Γ point to the X point [22]. Note that the SOC strongly modifies the electronic structure of the Bi compounds [FIGs. 1(c) and 5(a)] but has negligible effect on that of the In compound [FIG. 1(b)].

As quaternary compounds, Cs$_2$AgInCl$_6$, Cs$_2$AgBiCl$_6$, and Cs$_2$AgBiBr$_6$ have many competing binary and ternary phases. We performed thorough evaluation of thermodynamic stability via the phase stability diagram analysis. A quaternary compound has three independent elemental chemical potentials; thus, the stable region for the single-phase quaternary compound is a polyhedron in a three-dimensional chemical potential space. Several cross-sections of the polyhedron corresponding to different values of the Ag chemical potential are shown for Cs$_2$AgInCl$_6$, Cs$_2$AgBiCl$_6$ and Cs$_2$AgBiBr$_6$ [FIGs. 2 and 5(b)]. Our results indicate that all three compounds can be grown in single phases. The defect formation energies for the three HDPs were calculated using the elemental chemical potentials corresponding to the selected points in the phase diagram to evaluate the tunability of the defect concentrations and the Fermi level.

There are a large number of intrinsic point defects in quaternary HDPs. Vacancies are generally important in halides due to their low formation energies. On the other hand, the close-packed perovskite crystal structure usually causes high formation energies for metal interstitials unless the metal ion has a low charge state of +1 [56]. Antisite
defects in a multinary compound could be important except those due to substitution by an isovalent ion (i.e., A+ on B+ or B’+ on A’), which leads to an electrically inactive neutral defect, or by an ion with a drastically different oxidation state (i.e., B’3+ on X- and X’ on B’3+), which usually incurs high energy cost. For double perovskite halides, the antisite defects due to the disorder on B and B’ sites are likely abundant because of the same octahedral environment for both sites. The above considerations led us to investigate intrinsic defects in each of Cs₂AgInCl₆, Cs₂AgBiCl₆, and Cs₂AgBiBr₆, including four vacancies (V-Cs, V-Ag, V-In/V-Bi, and V-Cl/V-Br), six antisite substitutions (CsCl/CsCl, ClCs/BrCs, CsBr/CsBi, InCs/BiCs, AgIn/AgBi, and InAg/BiAg) and two interstitials (CsI and AgI).

Since the formation energy of a point defect depends on the chemical potentials of the constituent elements, we evaluated defect formation energies using the chemical potentials corresponding to a large number of points that sample the phase diagram. Representative points in the phase diagram [FIGs. 2 and 5(b)] were chosen to demonstrate the tunability of the defect concentration and the Fermi level [FIGs. 3-5]. Our calculations show that V-Ag is the most important acceptor defect while the halogen vacancy V-Cl/V-Br, the antisite defect InAg/BiAg, and AgI are important donor defects. The relative stability of the above three donor defects differ in the three compounds (Cs₂AgInCl₆, Cs₂AgBiCl₆, and Cs₂AgBiBr₆). On the other hand, V-Ag is the most stable acceptor defect in all three compounds even under the Ag-rich conditions [e.g., ∆μAg = 0.0 eV in FIG. 3(a)].

The results in FIG. 4 and S5 show that V-Ag is a shallow acceptor and AgI is a shallow donor in Cs₂AgInCl₆, Cs₂AgBiCl₆ and Cs₂AgBiBr₆. The antisite defects InAg (in Cs₂AgInCl₆) and BiAg (in Cs₂AgBiX₆) insert relatively deep (+2/+1) and the (+/0) levels inside the band gap. The halogen vacancy is shallow in Cs₂AgInCl₆ [FIG. 4(a)] but deep in Cs₂AgBiCl₆ [FIG. 4(b)] and Cs₂AgBiBr₆ (FIG. S5). The calculated (+/0) transition levels of the halogen vacancies in Cs₂AgInCl₆, Cs₂AgBiCl₆, and Cs₂AgBiBr₆ are 0.04 eV, 0.92 eV, and 0.35 eV below their respective CBM. The deeper (+/0) level of V-Cl in Cs₂AgBiCl₆ than in Cs₂AgInCl₆ may be understood by considering that Cs₂AgBiCl₆ has a...
larger band gap than Cs₂AgInCl₆; in addition, Bi⁴⁺ is a larger ion than In³⁺ and the Bi dangling bond is a Bi-6p orbital pointing directly towards V₃Cl, leading to strong hybridization between the Bi-6p and the Ag-5s orbitals at V₃Cl and consequently deeper electron trapping. Going from Cs₂AgBiCl₆ to Cs₂AgBiBr₆, the halogen vacancy size increases and consequently the Bi-Ag hybridization is weakened at the vacancy; therefore, the (+/0) level of V₁Br in Cs₂AgBiBr₆ (FIG. S5) is shallower than that in Cs₂AgBiCl₆ [FIG. 4(b)].

The electron trapping at halogen vacancies in the above three HDPs causes strong structural relaxation, which leads to the negative-U behavior in the case of V₃Br in Cs₂AgBiBr₆ with the (+/0) level above the (0/-) level. The Ag⁺ and the Bi³⁺ ions adjacent to the positively charged V₃⁺ repel each other. With successive addition of electrons to V₃⁺, the Ag-Bi distance is shortened to increase the hybridization and create a gap level that traps the electrons [57]. The calculated Ag-Bi distance at V₃Br in Cs₂AgBiBr₆ decreases from 5.90 Å, 3.03 Å, to 2.81 Å when the charge state of V₃Br is changed from +1, 0, to -1 (see FIG. S2). The Ag-Bi/In distance at V₃Cl in Cs₂AgInCl₆ and Cs₂AgInCl₆ also shows the same trend (TABLE S2).

Among the low-energy defects in Cs₂AgInCl₆, only the antisite defect InAg is a relatively deep donor defect [FIG. 3(a)]. This defect property is similar to that in Cs₂AgInBr₆ found in a previous DFT study [58]. In the two Bi HDPs, in addition to the antisite defect BiAg, the halogen vacancy is also a deep donor [FIGs. 3(b) and 5(c)]. Compared to halide single perovskites, the halide double perovskites introduce additional antisite defects, which can induce deep gap states as shown above. The deep donor defects (InAg in Cs₂AgInCl₆, BiAg and V₃Cl in Cs₂AgBiCl₆, and BiAg and V₃Br in Cs₂AgBiBr₆) are effective electron traps; thus, their concentrations need to be controlled.

By sampling the chemical potentials in the phase diagram, we find that combining the In/Bi-poor and the halogen-rich conditions suppresses the concentrations of the above deep electron trapping defects, [see, for example, the point C in FIG. 2(a) for Cs₂AgInCl₆, the point C in FIG. S3 for Cs₂AgBiCl₆, and the point A in FIG. S4 for Cs₂AgBiBr₆]. Due to the low growth temperature of HDPs (below 210 ºC for Cs₂AgBiX₆) [25],

![FIG. 3. The calculated formation energies of intrinsic defects in Cs₂AgInCl₆ (a, b, c) and Cs₂AgBiCl₆ (d, e, f), as a function of E₉, at three representative chemical potential points (A, B, and C) in FIG. 2. The slopes of the line segments indicate the defect charge](image-url)

FIG. 3. The calculated formation energies of intrinsic defects in Cs₂AgInCl₆ (a, b, c) and Cs₂AgBiCl₆ (d, e, f), as a function of E₉, at three representative chemical potential points (A, B, and C) in FIG. 2. The slopes of the line segments indicate the defect charge
states and the kinks denote the transition energy levels. The Fermi levels are referenced to the host VBM. The defects with high formation energies are plotted using dash lines.

The formation energies of near 0.8 eV or higher [at the pinned Fermi level in FIG. 3(c) (point C), FIG. S3 (point C), FIG. S4(b) (point A)] should lead to low concentrations of the above deep donors according to Eq.S1. Thus, the In/Bi-poor and the halogen-rich growth conditions may lead to improved electron transport efficiency in Cs₂AgInCl₆ and Cs₂AgBiX₆.

FIG. 4. The calculated transition energy levels for intrinsic donor (blue lines) and acceptor (red lines) defects in (a) Cs₂AgInCl₆ and (b) Cs₂AgBiCl₆, which are referenced to the host VBM (bottom dash lines).

Cs₂AgInCl₆ with low hole density may be attainable under the Cl-rich condition. Under this condition, the deep donor \( \mu_{Ag} \) has relatively high formation energy as shown in FIG. 3(c). The other low-energy donor defect \( V₃₋ \) is shallow and thus is not an effective electron trap. Hence, Cs₂AgInCl₆ is potentially useful as a \( p \)-type solar absorber material with long minority carrier lifetime. Semi-insulating Cs₂AgInCl₆ may also be used as a radiation detector material.

The location of the Fermi level in a semiconductor is important for PV and radiation detection applications. Without external doping, the Fermi level can be pinned by the lowest-energy donor and acceptor defects. Our calculations show that the Fermi levels in the three HDPs can vary in a wide range within the band gap depending on the chemical potentials of the constituent elements [see FIGs. 3(a)-(c), S1 for Cs₂AgInCl₆, FIGs. 3(d)-(f), S3 for Cs₂AgBiCl₆, and FIGs. 5 and S4 for Cs₂AgBiBr₆]. In Cs₂AgInCl₆, the Cl chemical potential is most effective in tuning the Fermi level. Cs₂AgInCl₆ is \( n \)-type under Cl-poor conditions [FIGs. 3(a)-(b)] and \( p \)-type under Cl-rich conditions [FIG. 3(c)]. Although the Fermi level is too deep in \( n \)-type Cs₂AgInCl₆, the Cl-rich conditions can move the Fermi level reasonably close to the VBM [about 0.3 eV above the VBM as shown in FIGs. 1(c) and S1]. Thus, \( p \)-type

FIG. 5. (a) Electronic band structure and orbital-projected density of states of Cs₂AgBiBr₆. (b) Calculated phase diagram at \( \Delta \mu_Ag = 0 \) eV, and \( \Delta \mu_Ag = -0.5 \) eV. The green regions indicate the stable region for single-phase Cs₂AgBiBr₆. (c) The calculated formation energies of intrinsic defects in Cs₂AgBiBr₆, as a function of \( E_F \), at the Point A (I) and the Point B (II) in the phase diagram (b). The slopes of the line segments indicate the defect charge states and the kinks denote the transition energy levels. The Fermi levels are referenced to the VBM of Cs₂AgBiBr₆.

The Fermi level of Cs₂AgBiCl₆ is confined within the \( p \)-type region based on our calculations [FIGs. 3(d)-(f) and S3]. The Cl-rich and the Bi-poor conditions (the point C in FIG. S3) can pin the Fermi level close to the VBM (0.18 eV above the VBM), leading to good \( p \)-type conductivity with high hole density. Under these conditions, the concentrations of the deep donors \( Bi_{Ag} \) and \( V_Cl \) are suppressed as discussed above. Therefore, similar to Cs₂AgInCl₆, Cs₂AgBiCl₆ may also be a potential \( p \)-type solar absorber material with long minority carrier lifetime. In contrast to Cs₂AgInCl₆ and Cs₂AgBiCl₆, the Fermi level of Cs₂AgBiBr₆ is more distanced away from both the CBM and the VBM (FIG. S4). This is consistent with the ob-
erved high resistivity in Cs$_2$AgBiBr$_6$ [36], which is required for a semiconductor radiation detection material. Since good carrier mobility and lifetime are also required for radiation detection, the combination of the Bi-poor and the Br-rich conditions (the point A in FIG. S4), which suppress the formation of the deep electron traps $V_{el}$ and Bi$_{AS}$, are desirable for Cs$_2$AgBiBr$_6$ detectors.

Using first principles calculations including spin-orbital coupling, we have systematically investigated the physical properties of defects in three representative HDPs, Cs$_2$AgInCl$_6$, Cs$_2$AgBiCl$_6$ and Cs$_2$AgBiBr$_6$ as promising optoelectronic materials. Detailed calculations of the formation energies and transition levels of intrinsic defects lead to the following important findings: (i) Bi$_{AS}$ and halogen vacancies in Cs$_2$AgBiCl$_6$ and Cs$_2$AgBiBr$_6$ as well as In$_{AS}$ in Cs$_2$AgInCl$_6$ are identified as deep electron traps with low formation energies and require Bi/In-poor and halogen-rich conditions to suppress; (ii) The Fermi level in three HDPs can be tuned by modifying the chemical potentials of their constituent elements (or equivalently the growth conditions). Cs$_2$AgInCl$_6$ and Cs$_2$AgBiCl$_6$ can both be $p$-type with the latter having higher attainable hole density while Cs$_2$AgBiBr$_6$ is usually semi-insulating with high resistivity; (iii) Based on the above results, Cs$_2$AgInCl$_6$ and Cs$_2$AgBiCl$_6$ may be potentially useful as $p$-type solar absorbers with good minority carrier lifetimes or as photon detectors while Cs$_2$AgBiBr$_6$ is a promising semiconductor radiation detection material. Our work provides valuable guidelines for further exploration of Pb-free perovskites for diverse applications.

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* Mao-Hua Du: mhdu@ornl.gov  
* Lijun Zhang: lijun_zhang@jlu.edu.cn

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Supplemental Material for “Intrinsic defect properties in halide double perovskites for optoelectronic applications”

Tianshu Li,¹ Xingang Zhao,¹ Dongwen Yang,¹ Mao-Hua Du,²,* and Lijun Zhang¹,*

¹State Key Laboratory of Superhard Materials, Key Laboratory of Automobile Materials of MOE, and College of Materials Science and Engineering, Jilin University, Changchun 130012, China.

²Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States.

I. Detailed description on defect calculations.

The probability of the formation of an intrinsic defect is determined by its formation energy. For a point defect $D$ in the charge state $q$, its equilibrium concentration in a crystal is given by

$$c(D,q) = \frac{N_{site}}{g_q} \exp\left[\frac{-\frac{E'(D^q)}{k_BT}}{q}\right]$$

(1)

where $k_B$ is the Boltzmann constant, $T$ is the temperature, $E'(D^q)$ is the formation energy, $N_{site}$ is the number of possible atomic sites at which the defect may be formed, $g_q$ is the degeneracy factor for charge state $q$, which equals to the number of possible structural configurations and electron occupancies. The formation energy of a point defect can be evaluated as

$$E'(D^q) = (E^q_D - E_i) - \sum_i n_i (\mu_i + \mu^{bulk}_i) + q (\epsilon_{VBM} + \epsilon_f) + \Delta E_{corr}$$

(2)

where $E^q_D$ is the total energy of the defect at the charge state $q$ in the supercell, $E_i$ is the energy of the defect-free supercell and $n_i$ is the difference in the number of atoms for the $i$th atomic species between the defect-containing and defect-free supercells. $\mu_i$ is the chemical potential of the $i$th atomic species relative to its bulk chemical potential $\mu_i^{bulk}$. $\epsilon_{VBM}$ is the energy of valence-band maximum (VBM) of the defect-free material and $\epsilon_f$ is the Fermi energy referenced to $\epsilon_{VBM}$. The last term $\Delta E_{corr}$ corrects the error caused by the finite size of the supercell, including the image charge correction and the potential alignment correction [51-55]. The thermodynamic transition energy between two charge states $q$ and $q'$ can be determined by

$$\epsilon(q,q') = \frac{[E'(D,q;\epsilon_f=0) - E'(D,q';\epsilon_f=0)]}{(q-q')}$$

(3)

when the Fermi level is below this energy, the charge state $q$ is stable; otherwise, the charge state $q'$ is stable.

For the HSE+SOC calculations of defects, we used only one k point (Γ point) due to the high computational cost. The convergence test performed at the PBE level shows that using a denser $2 \times 2 \times 2$ k-point mesh increases the formation energies of the Cl vacancy ($V_{Cl}$) at the +1 and neutral charge states in Cs$_2$AgBiCl$_6$ by 0.11 eV and 0.15 eV, respectively, which results in an increase of the (+/0) transition level of $V_{Cl}$ by only 0.04 eV. This test shows that the error due to the k-point mesh is small and should not affect the conclusions of this paper.
II. Supplementary Tables and Figures.

TABLE S1. Comparison of the crystal system, space group, lattice parameters and band gaps between calculated and experimental results for Cs$_2$AgInCl$_6$, Cs$_2$AgBiCl$_6$ and Cs$_2$AgBiBr$_6$.

|                  | Cs$_2$AgInCl$_6$ | Cs$_2$AgBiCl$_6$ | Cs$_2$AgBiBr$_6$ |
|------------------|------------------|------------------|------------------|
| Crystal system   | Cubic            | $Fmar{3}m$      |                  |
| Space group      |                  |                  |                  |
| a (Å) (Calc.)    | 10.68            | 10.96            | 11.48            |
| a (Å) (Exp.)     | 10.47[39]        | 10.78[29]        | 11.26[29]        |
| Band gap (eV) (Calc.) | 2.36          | 2.72             | 2.18             |
| Band gap (eV) (Exp.) | 2.00[39]      | 2.20-2.77[25,42] | 1.83-2.19[42]   |

TABLE S2. The In/Bi-Ag distances at halogen vacancies of different charge states in Cs$_2$AgInCl$_6$, Cs$_2$AgBiCl$_6$ and Cs$_2$AgBiBr$_6$.

|                  | Cs$_2$AgInCl$_6$ | Cs$_2$AgBiCl$_6$ | Cs$_2$AgBiBr$_6$ |
|------------------|------------------|------------------|------------------|
| Charge $+_1$     | 5.75 (Å)         | 5.61 (Å)         | 5.90 (Å)         |
| Charge $-_1$     | 2.74 (Å)         | 2.82 (Å)         | 2.81 (Å)         |
| Charge $-_0$     | 5.65 (Å)         | 3.48 (Å)         | 3.03 (Å)         |

FIG. S1. (Left) Calculated phase diagram of Cs$_2$AgInCl$_6$ at $\Delta \mu_{\text{Ag}}=-2.0$eV. The green region indicates the stable region for the single-phase Cs$_2$AgInCl$_6$. (Right) The formation energies of dominant intrinsic defects as a function of $E_F$ at the Point A in the phase diagram in Cs$_2$AgInCl$_6$. The slopes of the line segments indicate the defect charge states and the kinks denote the transition energy levels. The Fermi levels are referenced to the host VBM.
FIG. S2. The local structures of the Br vacancy at -1 (a), neutral (b), and +1 (c) charge states in Cs$_2$AgBiBr$_6$.

FIG. S3. The calculated formation energies of dominant intrinsic defects in Cs$_2$AgBiCl$_6$ at three chemical potential points A, B and C under Bi-poor growth conditions. The slopes of the line segments indicate the defect charge states and the kinks denote the transition energy levels. The Fermi levels are referenced to the host VBM.

FIG. S4. (a) Calculated phase diagram of Cs$_2$AgBiBr$_6$ at $\Delta \mu_{Ag} = -1.0$eV. The green region indicates the stable region for the single-phase Cs$_2$AgBiBr$_6$. (b) The formation energies of dominant intrinsic defects as a function of $E_F$ at the Points A (left) and B (right) in...
Cs$_2$AgBiBr$_6$. The slopes of the line segments indicate the defect charge states and the kinks denote the transition energy levels. The Fermi levels are referenced to the host VBM.

FIG. S5. The calculated transition energy levels for intrinsic donor (blue lines) and acceptor (red lines) defects in Cs$_2$AgBiBr$_6$, which are referenced to the VBM (bottom dash lines).

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