

Intrinsic doping limitations in inorganic lead halide perovskites†

Cite this: *Mater. Horiz.*, 2022, 9, 791

   ^a Al ^x  ^b   ^{*a}

Inorganic halide perovskites (HP's) of the CsPbX₃ (X = I, Br, Cl) type have reached prominence in photovoltaic solar cell efficiencies, leading to the expectation that they are a new class of semiconductors relative to the traditional ones. Peculiarly, they have shown an asymmetry in their ability to be doped by holes vs. electrons. Indeed, both structural defect-induced doping as well as extrinsic impurity-induced doping strangely often result in HP's in a unipolar doping (dominantly p-type) with low free carriers' concentration. This raises the question whether such doping limitations presents just a temporary setback due to insufficient optimization of the doping process, or perhaps this represents an intrinsic, physically-mandated bottleneck. In this paper we study three fundamental Design Principles (DP's) for ideal doping, applying them via density functional doping theory to these HP's, thus identifying the violated DP that explains the doping limitations and asymmetry in these HP's. Here, the target DP are: (i) requires that the thermodynamic transition level between different charge states induced by the dopants must ideally be energetically shallow both for donors (n-type) or acceptors (p-type); DP-(ii) requires that the 'Fermi level pinning energies' for electrons $E_{\text{pin}}^{(n)}$ and holes $E_{\text{pin}}^{(p)}$ (being the limiting value of the Fermi level before a structural defect that compensate the doping forms spontaneously) should ideally be located inside the conduction band for n-type doping and inside the valence band for p-type doping. DP-(iii) requires that the doping-induced shift in equilibrium Fermi energy $\Delta E_{\text{F}}^{(n)}$ towards the conduction band for n-type doping (shift of $\Delta E_{\text{F}}^{(p)}$

the E_c (E_v)

to n-type doping. The results that support the p-type doping are obtained from the literature.^{5,16,30,31} Thus, the following dopant elements are calculated only in the Pb site: I, Ga, In, Sb, Bi, La and Cu. The formation energy for dopant on Cs site or interstitial are very high because the large difference in the atomic radius, and therefore were not considered. The thermodynamic transition levels (TTL) of these defects and dopants are calculated with eqn (2), and these points are mentioned and highlighted in the Results section.

() : To compute the total energy used in the eqn (1), and all the electronic properties of HP's we used first principles calculations based on density functional theory (DFT) as implemented in Vienna *Ab* Simulation Package – VASP.^{32,33} The projected augmented wave method (PAW)^{34,35} was employed to describe the interaction of valence electrons with the ionic cores, considering the following electronic distribution for each chemical specie: I ($3s^2 3p^1$), Cu ($5d^{10} 6s^1$), Br ($4s^2 4p^5$), Bi ($6s^2 6p^3$), Cl ($3s^2 3p^5$), Cs ($5s^2 5p^6 6s^1$), Ga ($4s^2 4p^1$), In ($5s^2 5p^5$), La ($6s^2 5d^1$), Pb ($6s^2 6p^2$), Sb ($5s^2 5p^3$). For the exchange and correlation functional we employed the Perdew–Burke–Ernzerhof implemented for solid materials (PBEsol)³⁶ and the stress tensor and the atomic forces were minimized with a plane wave energy cutoff of 400 eV. Also we used a Γ -point mesh of $5 \times 5 \times 9$ to integrate the Brillouin zone of CsPbBr₃ in the primitive orthorhombic cell and the same density for all the remaining systems.

The band gaps of CsPbX₃ (X = Cl, Br, I) o6636c8o22290Tc6.n.7826317.2534T-g.220i5.97nTm(5pc8.9663008.9)-3871Td((5)63008.9T4(610005.976853(h

conditions respectively. However, when the dopant is incorporated in the system, the thermodynamic stability condition should avoid the precipitation of the doping precursor or the formation of other compounds. If we consider the precursors of the dopants in the halogen base (for example, to dope CsPbI

p-type pinning energy $E_{\text{pin}}^{(p)}$ in CsPbCl₃ lies in the valence band, however the doping-induced Fermi energy shift $\Delta E_{\text{F}}^{(p)}$ towards the valence band after doping with acceptor impurities such as Na, K, Rb, Cu or Mg is still far away from the valence band maximum, lying deep in the band gap.⁵ The $\Delta E_{\text{F}}^{(p)}$ is very small and makes the p-type doping unsuccessful.

The DPs (ii) and (iii) are a consequence of the valence and conduction band position with respect to the vacuum. When the atomic radius of halogen decreases, *i.e.*, goes from I to Cl, the position of E_{v} tends to become deeper in energy, increasing the ionization potential for the HP's, as shown in Fig. S3 in the ESI.^{†43} High ionization potential increases the difficulty to find shallow acceptors that leads to a large $\Delta E_{\text{F}}^{(p)}$ and therefore the p-type doping becomes unlikely to be achieved. For the n-type, the decrease in the halogen radius also decrease the electronic affinity of the halide perovskite, and the E_{c} becomes closer to the vacuum level for Cl when compared to I or Br, as shown in Fig. S3 in ESI.^{†43} Thus, the difficulty to find shallow donors that leads to large $\Delta E_{\text{F}}^{(n)}$ increases and the process to achieve the n-type doping becomes unlikely.

In the next section, through DFT calculations, we determine the Fermi pinning levels and $\Delta E_{\text{F}}^{(n)}$ and $\Delta E_{\text{F}}^{(p)}$ for CsPbX₃ (X = I, Br and Cl), that is the base for our DP already demonstrated. In addition, we discuss the details of atomic configuration and electronic properties for each defect and dopant.

IV. Structural defects and extrinsic impurities as dopants

considered as a shallow donor. In contrast, for CsPbCl₃ the TTL (+/-) for V_X lies at $E_c - 0.30$ eV, which is nearly a deep donor.

: Being highly ionic, the Cs vacancy does not lead to dangling bonds in the structure. Instead, they leave one hole in the valence band which is derived from halogen X p-orbitals.⁴⁴ Different from the oxides perovskites, such as SrTiO₃, the hole does not tend to form a polaron.⁴⁵

In all HP's studied here, we observed that the Cs vacancy has the 1- (V_{Cs}¹⁻) charge state with the lowest formation energy. Other tested charge states (e.g., neutral and 1+) have higher formation energies. Because of that, V_{Cs} is considered a shallow acceptor defect and act as a source of electron compensation in CsPbX₃ (X = Cl, Br, I). The formation energy of V_{Cs}¹⁻ has negative values for a wide range of E_F , especially close to the conduction band. This result is independent of the halogen chemical specie despite the intensity is larger for X = Cl. The main reason for that is associated to the larger (smaller) ionic potential (electron affinity) of CsPbCl₃ that pushes the E_v (E_c) to deeper (shallow) energies when compares to the vacuum level, as shown in Fig. S3 in the ESI.†

: When the Pb vacancy is introduced in CsPbX₃ (X = Cl, Br, I), six Pb-X bonds are broken and two holes are left in the valence band. Similar to V_{Cs}, those two holes do not tend to localize and form small polarons. The distance of two neighboring halogen atoms is so large that the X-X bond is avoided for X = Br and Cl. Nevertheless, the largest atomic radius of I (compared to Cl and Br) results in a larger interaction of the halogen atoms leading to a formation of a trimer I-I-I inside the V_{Pb} by a dislocation of one I atom. This atomic configuration is observed only in the neutral charge state, V

interaction, and is the deep intrinsic defect with the smallest formation energy.

The shift of the thermodynamic charge transition level (+/-) towards the E_v when the halogen changes from I_i to Br_i (and also the instability of $1+$, when compared to $1-$, in $CsPbCl_3$) is associated with the increase of the formation energy of the $1+$ charge state. When the radius of the halogen atom increases, it allows the formation of a trimer $X-X-X$ due to the larger space

the p orbitals. When this impurity replaces Pb in CsPbX₃ (X = Cl, Br, I), two electrons tend to be donated to halogen atoms and one unpaired electron in the s orbital is observed in the neutral charge state. This configuration with half of the s orbitals filled has a very high formation energy, and therefore is less stable than the 1+ or 1- charge state, as shown in the formation energy diagrams depicted in Fig. 5 (light blue, green and pink lines). As discussed for V_X and X_i, these elements from the III family (substitutional at the Pb site) show a negative Coulomb interaction (negative U), .e., the elements Bi, Ga and In tend to form a completely full or empty s orbital, and by consequence only the transition from 1+ to 1- charge state is observed.

For Bi doping, the transition (+/-) occurs only inside the conduction band, which makes this element a shallow donor. However, the formation energy of this defect is very high, and comparable to the most stable intrinsic donor defect (V_X). Even though the TTL indicates a good candidate for n-type doping, the large formation energy discards the usability of Bi. The incorporation of Ga on Pb site, Ga_{Pb}, has a similar formation energy as Bi_{Pb} for all the halide perovskites studied here, however the TTL (+/-) occurs deep inside the band gap. This behavior indicates that Ga_{Pb} act as electron compensation defect when the Fermi level lies closer to the E_c, and therefore cannot be considered a good candidate for n-type doping. Despite the formation energy of In_{Pb} is smaller than Ga_{Pb}, especially in CsPbCl₃, the deep TTL inside the band gap leads to the same n-type charge compensation of Ga_{Pb} and therefore is considered a poor candidate for n-type doping in CsPbX₃ (X = Cl, Br, I).

A: Sb and Bi have five valence electrons: two electrons in the s orbitals and three in the

p orbitals. This electronic configuration can make Bi and Sb to have two possible formal oxidation states: 5+ and 3+. When these elements replace Pb in the octahedral site, only the oxidation state 3+ can be observed, thus two valence electrons from the p orbital are donated to halogen atoms and only one unpaired electron in the p orbital (with the two in s orbitals) compose the neutral charge condition for Bi and Sb substitutional defects. This configuration has a high formation energy and is more stable than the charged defects for a small window close to the E_c for Sb in all CsPbX₃ (X = Cl, Br, I) as shown by the horizontal brown line in Fig. 5. For Bi atom, a negative Coulomb interaction is observed only for CsPbI₃, while the formation energy for neutral charge state is the lowest one compared to the charged for X = Cl and Br close to E_c. The main reason for the stability of the neutral charge state (one unpaired electron in the p-orbital) is that the atomic configuration does not change too much when the charge state varies from 1- to 0 and from 0 to 1+ with these substitutional atoms. This results in an energy gain for atomic relaxation smaller than the other examples shown here, such as V_X and substitutional atoms from family III .

The formation energy for Bi and Sb in CsPbBr₃ and CsPbI₃ has a negative value for most available electronic chemical potentials (Fermi energy): from close to E

: The substitution of Pb by La leads to a much larger formation energy for neutral and negative charge states if compared to the positive one for all CsPbX₃ (X = Cl, Br, I) perovskites. The donation of two valence electrons (one from d and one from s orbitals) of La to halogen atoms leaves one unpaired electron in the s orbital that increases its formation energy, resulting in a decreased stability when compared to the positive configuration. The transition level (+/-) occurs only deep inside the conduction band for all CsPbX₃ (X = Cl, Br, I). In the intermediate condition (point), the formation energy of La_{Pb}¹⁺ is negative only close to the E_v

band should not have a small electron affinity. When a material does not follow these points, issues are observed such as the possibility for charge localization in form of small polarons, and pinning for holes or electrons that lie inside the band gap, DP-(ii). Taking as examples oxides and nitrates, it is known that they are very difficult to be doped as p-type because the valence band (composed by O or N p orbitals) lies very deep in energy, which also can induce the formation of small polarons.^{22,47-49} For halide perovskites based on Cl the band gap is wide,

- 14 X. Zhang, J.-X. Shen, M. E. Turiansky and C. G. V. de Walle, *J. Mater. Chem. A*, 2020, **8**, 12964–12967.
- 15 S. Mannodi-Kanakkithodi, J.-S. Park, B. F. Martinson and M. K. Y. Chan, *J. Phys. Chem. C*, 2020, **124**, 16729–16738.
- 16 S. Zhou, Y. Ma, G. Zhou, X. Xu, M. Qin, Y. Li, Y.-J. Hsu, H. Hu, G. Li, N. Zhao, J. Xu and X. Lu, *ACS Energy Lett.*, 2019, **4**, 534–541.
- 17 C. Freysoldt, J. Neugebauer and C. G. Van de Walle, *Phys. Rev. Lett.*, 2009, **102**, 016402.
- 18 C. Freysoldt, J. Neugebauer and C. G. V. de Walle, *Phys. Status Solid B*, 2011, **248**, 1067–1076.
- 19 S. Zunger, *Appl. Phys. Lett.*, 2003, **83**, 57–59.
- 20 S. Zunger and O. I. Malyi, *Chem. Rev.*, 2021, **121**, 3031–3060.
- 21 S. B. Zhang, S.-H. Wei and S. Zunger, *Phys. Rev. Lett.*, 2000, **84**, 1232–1235.
- 22 J. L. Lyons, S. Janotti and C. G. Van de Walle, *Phys. Rev. Lett.*, 2012, **108**, 156403.
- 23 S. Bonadio, C. Escanhoela, F. P. Sabino, G. Sombrio, V. G. de Paula, F. F. Ferreira, S. Janotti, G. M. Dalpian and J. Souza, *J. Mater. Chem. A*, 2021, **9**, 1089–1099.
- 24 R. Lim and S.-Y. Jeong, *Solid State Chem.*, 1999, **110**, 131–136.
- 25 M. Sebastian, J. Peters, C. C. Stoumpos, J. Im, S. S. Kostina, Z. Liu, M. G. Kanatzidis, J. Freeman and B. W. Wessels, *Phys. Rev. B: Condens. Matter Phys.*, 2015, **92**, 235210.
- 26 M. R. Linaburg, E. T. McClure, J. D. Majher and P. M. Woodward, *Chem. Mater.*, 2017, **29**, 3507–3514.
- 27 D. M. Trots and S. V. Myagkota, *J. Phys. Chem. Solid*, 2008, **69**, 2520–2526.
- 28 L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, J. Walsh and M. V. Kovalenko, *Nature Lett.*, 2015, **15**, 3692–3696.
- 29 D. Meggiolaro and F. De Angelis, *ACS Energy Lett.*, 2018, **3**, 2206–2222.
- 30 Y. Zhou, J. Chen, O. M. Bakr and H.-T. Sun, *Chem. Mater.*, 2018, **30**, 6589–6613.
- 31 X. Zhang, Q. Ma, R. Li, C. Lin, D. Huang and Y. Cheng, *J. Appl. Phys.*, 2021, **129**, 165110.
- 32 G. Kresse and J. Hafner, *Phys. Rev. B: Condens. Matter Phys.*, 1993, **48**, 13115–13118.
- 33 G. Kresse and J. Furthmüller, *Phys. Rev. B: Condens. Matter Phys.*, 1996, **54**, 11169–11186.
- 34 G. Kresse and D. Joubert, *Phys. Rev. B: Condens. Matter Phys.*, 1999, **59**, 1758–1775.
- 35 P. E. Blöchl, *Phys. Rev. B: Condens. Matter Phys.*, 1994, **50**, 17953–17979.
- 36 J. Perdew, S. Ruzsinszky, G. I. Csonka, O. Vydrov, G. E. Scuseria, L. Constantin, X. Zhou and K. Burke, *Phys. Rev. Lett.*, 2008, **100**, 136406.
- 37 L. Octavio de Araujo, F. P. Sabino, C. R. C. Rêgo and D. Guedes-Sobrinho, *J. Phys. Chem. Lett.*, 2021, **12**, 7245–7251.
- 38 M.-H. Du, *J. Phys. Chem. Lett.*, 2015, **6**, 1461–1466.