Electronic Supplementary Material (ESI) for Materials Horizons.

Supplementary Material: Intrinsic doping limitations in inorganic lead halide perovskites

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Chemical potentials for dopant atoms

One way to introduce impurities in halide perovskites is to mix the precursors of dopant atoms (in small concentration) with the precursor of the metal that goes to the B site of perovskite (ABX_3). For example, to introduce Bi in $CsPbBr_3$, the precursor $BiBr_3$ is added to $PbBr_2$. Considering this condition, and since we are analyzing the possible *n*-type dopants in the Pb site of $CsPbX_3$ (X = Cl, Br, I), the most stable precursors used are bonded with the halogens atoms. In addition, most of the impurity atoms studied here show a valence +3 (Al, Ga, In, Sb, Bi and La), resulting in a chemical formula for the precursor MX_3 (M = Al, Ga, In, Sb, Bi, La, Au and X = Cl, Br, I). The unique exception is AuI, that is more stable than the AuI_3. Thus, the chemical potential for the impurity can be calculated according to the formula (not considering AuI):

$$\mu_M + 3\mu_X < \Delta H_f(MX_3)\ (M\ =\ \mathrm{Al, Ga, In, Sb, Bi, La\ and\ Au\ and}\ X\ =\ \mathrm{Cl, Br, I}),$$

where μ_M is the chemical potential for the impurity atom and μ_X is the halogen chemical potential determined in the phase diagram shown in Fig. 2. Since the chemical potential should be smaller than 0 (using the isolated molecule of the halogen and the metallic bulk system as a reference), the chemical potential for each impurity can be limited by the halogen chemical potential. In other words, if this inequation is not satisfied, the precursor used to dope the halide perovskite will precipitate and the atoms are not going to be incorporated in the system.

To check the limit for the halogen chemical potential that leads to the incorporation of the dopant atoms in the system we calculate the formation energy of a substitution metal M on Pb site using the following expression (specific representation of Eq. (1) from the main text):

$$\Delta \mathrm{H}_f(\mathrm{M_{Pb}}, q) = E_{tot}(\mathrm{M_{Pb}}, q) - E_{tot}^{bulk} + \mu_{\mathrm{Pb}} - \mu_{\mathrm{M}} + qE_F + \Delta^{(q)} \qquad (1)$$

where $E_{tot}(\mathrm{M_{Pb}}, q)$ is the total energy of the system with the extrinsic defect metal M on Pb site, E_{tot}^{bulk} is the total energy of the system without the extrinsic impurity, μ_{Pb} and μ_{M} are the chemical potential for Pb and metal M, respectively, E_F is the parametric Fermi energy and $\Delta^{(q)}$ is the charge correction due to the finite size of the supercell. In this expression we need to rewrite the chemical potential of Pb and metal M as a function of the halogen chemical potential. For a more illustrative example, we consider here the system $CsPbI_3$, where the chemical potentials of all atoms for the perovskite stability follow the line of PbI_2, as shown in Fig. 2 of the main manuscript and Fig. S4 in the supplementary material. For all the other system, the chemical potential in the vicinity of $PbBr_2$ or $PbCl_2$ leads to an instability of the perovskite, however the trend of the formation energy vs. halogen chemical through the line B-C will be exactly the same as will be demonstrate for $CsPbI_3$.

We need to consider the extreme condition for the instability of the precursors used to grow and dope the HP's, i.e., PbI_2 and MX_3. It is important to mention that we considered the most used precursors for the system with trivalent oxidation states, such as Bi, Sb, In, Al, Ga, La and Au (with the exception of AuI that is more stable than AuI_3). Therefore, the equation in limit of precursors instability can be written as:

$$\mu_{\mathrm{Pb}} + 2\mu_{\mathrm{I}} = \Delta H_f(\mathrm{PbI_2}) \tag{2}$$

$$\mu_{\mathrm{M}} + 3\mu_{\mathrm{I}} = \Delta H_f(\mathrm{MI_3}). \tag{3}$$

Isolating the chemical potentials of Pb and the metal M of Eq. 2 and 3, respectively, replacing in the Eq. 1 and considering $E_F = 0$, we have:

$$\Delta \mathrm{H_f}(\mathrm{M_{Pb}}, q) = E_{tot}(\mathrm{M_{Pb}}, q) - E_{tot}^{bulk} + \Delta H_f(\mathrm{PbI_2}) - \Delta H_f(\mathrm{MI_3}) + \Delta^{(q)} + \mu_{\mathrm{I}}\ . \tag{4}$$

All of the terms shown in the Eq. 4 are constant, with the exception of the μ_{I} that is the halogen chemical potential. The halogen chemical potential is a negative number that lies in the range of: $\Delta H_f(\mathrm{MI_3})/3 < \mu_{\mathrm{I}} < [\Delta H_f(\mathrm{PbI_2}) + \Delta H_f(\mathrm{CsI_3}) - \Delta H_f(\mathrm{CsPbI_3})]/2$. The Eq.4 is plotted in the Fig. S1 for all the extrinsic metal dopants. When the halogen chemical potential is smaller than $\Delta H_f(\mathrm{MI_3})/3$, close to the halogen poor condition, the precipitation of the precursor of the impurity occur. This condition is represented by the abrupt discontinuity of the lines shown in Fig. S1 in SI. Despite the formation energy of M_{Pb} is smaller at $E_F = 0$ in the halogen poor chemical potential, this condition favors the precipitation of the precursor, which leads to a low incorporation of the extrinsic metal. This is a competition mechanism between the formation of M_{Pb} in HP's and the precipitation of MX_3. In addition, from Eq. 4 is clear that the formation energy of the dopant decrease when the halogen chemical potential goes from a rich to poor condition at $E_F = 0$, however, close to the equilibrium Fermi level, the formation energy of these dopant is almost constant for all possible halogen chemical potential. Going from halogen rich to halogen poor, the equilibrium Fermi level shift from valence band region toward the conduction band and the decrease of the formation energy at $E_F = 0$ is compensated at the equilibrium Fermi level. It is important to mention, that the trend demonstrated for $CsPbI_3$ will be exactly the same for $CsPbB_3$ and $CsPbCl_3$.

To plot Fig. 5, we consider a halide chemical potential that leads to an incorporation of all the dopant elements studied here, and indicated by the dashed line in Fig. S1 in almost the middle of the available region. This chemical potential corresponds to an intermediate halogen chemical potential shown by the point A in Fig. 2 of the main manuscript.

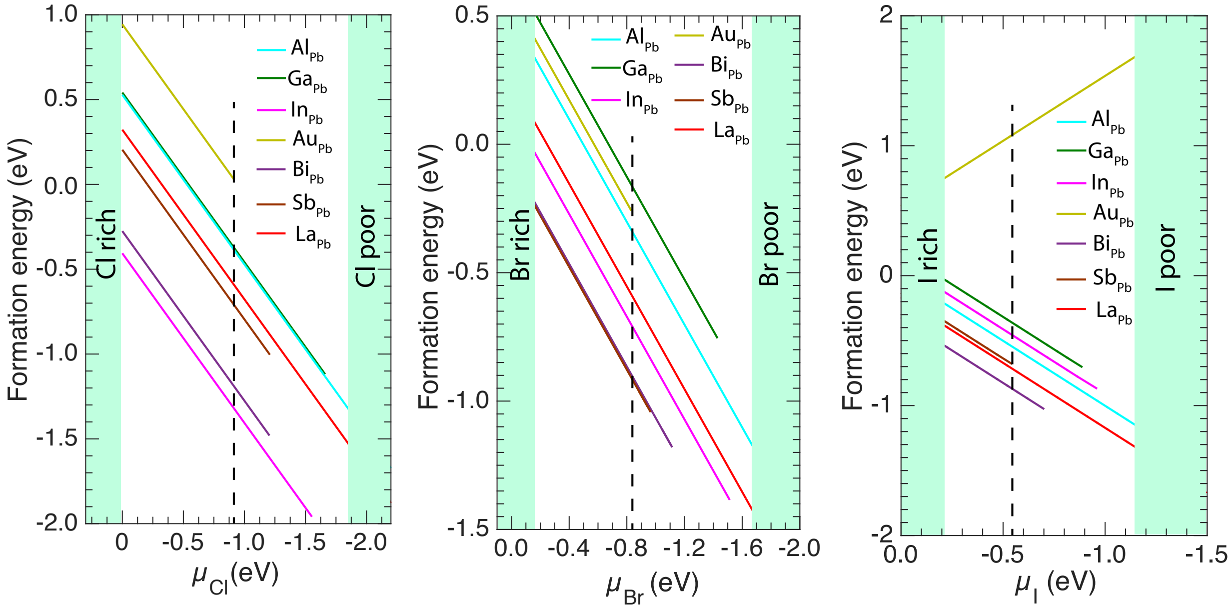
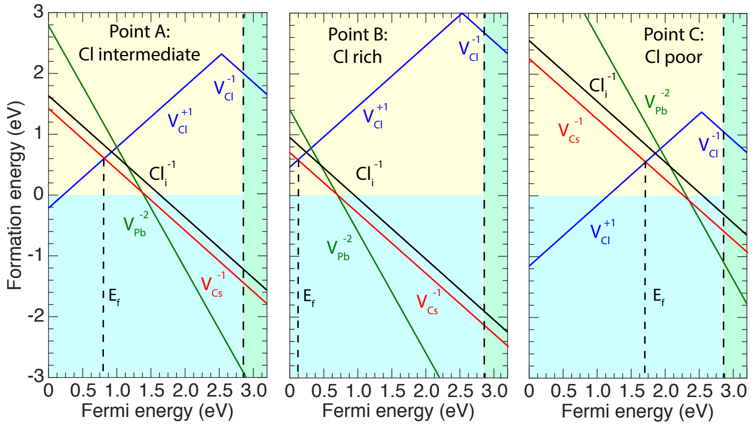
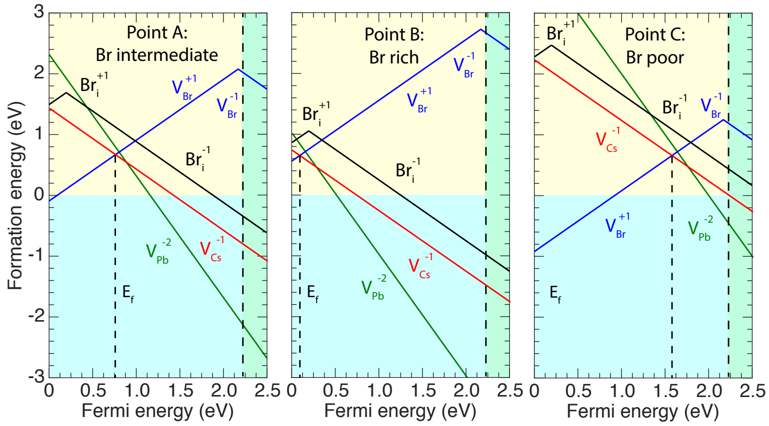


Fig S1. Formation energy as function of halogen chemical potential for substitutional Al, Ga, In, Sb, Bi, La and Au in Pb site. This energy refers to a condition of fermi energy $E_F = 0$ (valence band maximum).

Formation Energy of intrinsic defects


a) $CsPbCl_3$


b) $CsPbBr_3$

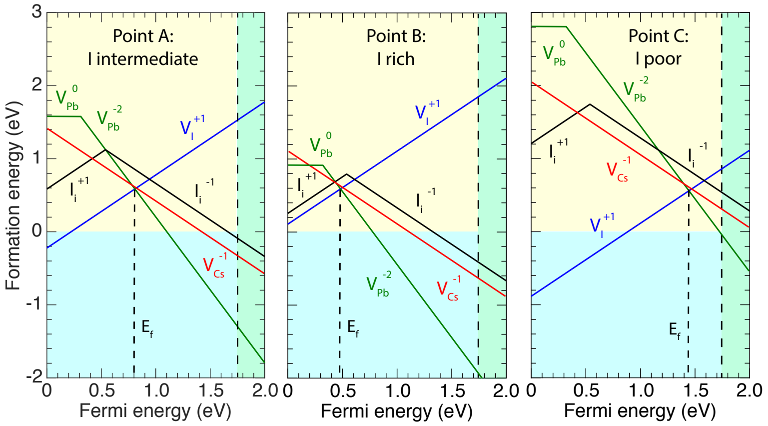

c) $CsPbI_3$

Fig. S2: Formation energy for intrinsic defects as a function of Fermi level for $CsPbX_3$ with a) X = Cl, b) X = Br and c) X = I. The formation energies were calculated for points A, B and C, which are shown in the phase diagram of Fig. 2 of the main manuscript. The limit for the conduction band is shown by the green area in each system (note different band gap scales for each compound). The blue and yellow areas represent the spontaneous and non-spontaneous formation energy of defects. The equilibrium Fermi level was determined by the crossing of the most stable acceptor and donor defects.

Shift in the Fermi level by the impurity incorporation

Table S1: Formation energy of dopant atoms, $\Delta\mathrm{H}_f$, in Pb site and in the Fermi level position determined by the crossing of M_{Pb}^{+1} and the most stable intrinsic acceptor defect ($\mathrm{V}_{\mathrm{Pb}}^{-2}$ou $\mathrm{V}_{\mathrm{Cs}}^{-1}$). The shift in doping-induced Fermi level generated by the dopant, $\Delta\mathrm{E}_{\mathrm{F}}^{(\mathrm{n})}$, was calculated in the halogen intermediated chemical potential (Point A in Fig. 2).

	$CsPbI_3$		$CsPbBr_3$		$CsPbCl_3$	
Impurities	$\Delta\mathrm{H}_f$ (eV) in E_F	$\Delta\mathrm{E}_{\mathrm{F}}^{(\mathrm{n})}$ (eV)	$\Delta\mathrm{H}_f$ (eV) in E_F	$\Delta\mathrm{E}_{\mathrm{F}}^{(\mathrm{n})}$ (eV)	$\Delta\mathrm{H}_f$ (eV) in E_F	$\Delta\mathrm{E}_{\mathrm{F}}^{(\mathrm{n})}$ (eV)
Al_{Pb}	0.38	0.11	0.53	0.09	0.57	0.15
Ga_{Pb}	0.52	0.04	0.65	0.03	0.57	0.15
In_{Pb}	0.44	0.08	0.29	0.21	-0.02	0.49
Sb_{Pb}	0.29	0.15	0.15	0.28	0.38	0.28
Bi_{Pb}	0.16	0.22	0.15	0.28	0.06	0.44
La_{Pb}	0.26	0.16	0.37	0.18	0.46	0.24

Alignment of impurity TTL with respect to host crystal band edges

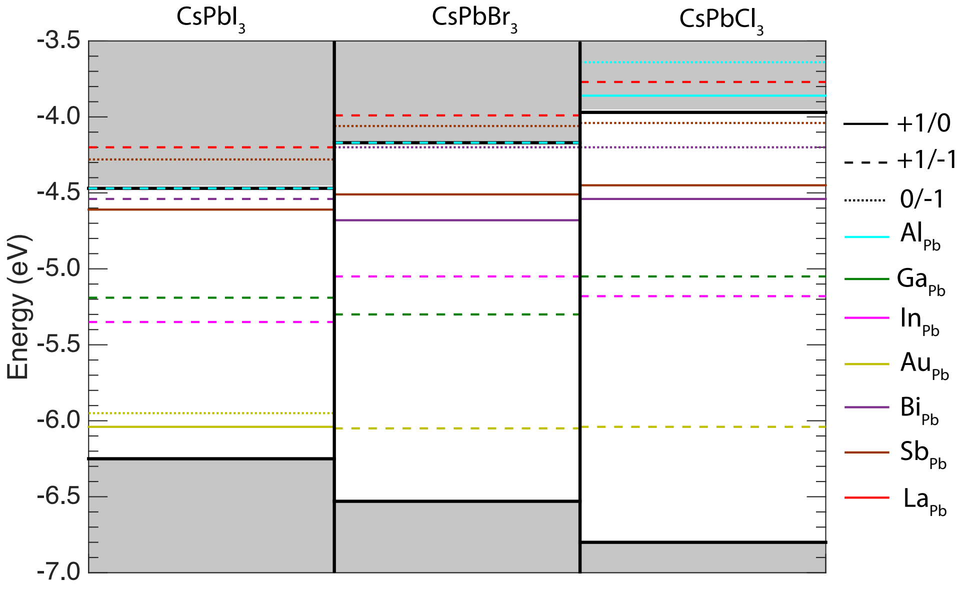


Fig. S3: Thermodynamic transition levels (TTL) in $CsPbX_3$ (X = Cl, Br, I) represented in the schematic band diagram with respect to the vacuum level. The valence band maximum are aligned according to Tao *et al.* results.[1] We can observe that the TTL are almost independent of the perovskite system, because the distance to the vacuum is very similar in all possible halogens *X* atoms.

Full Stability domains in the space of chemical potentials

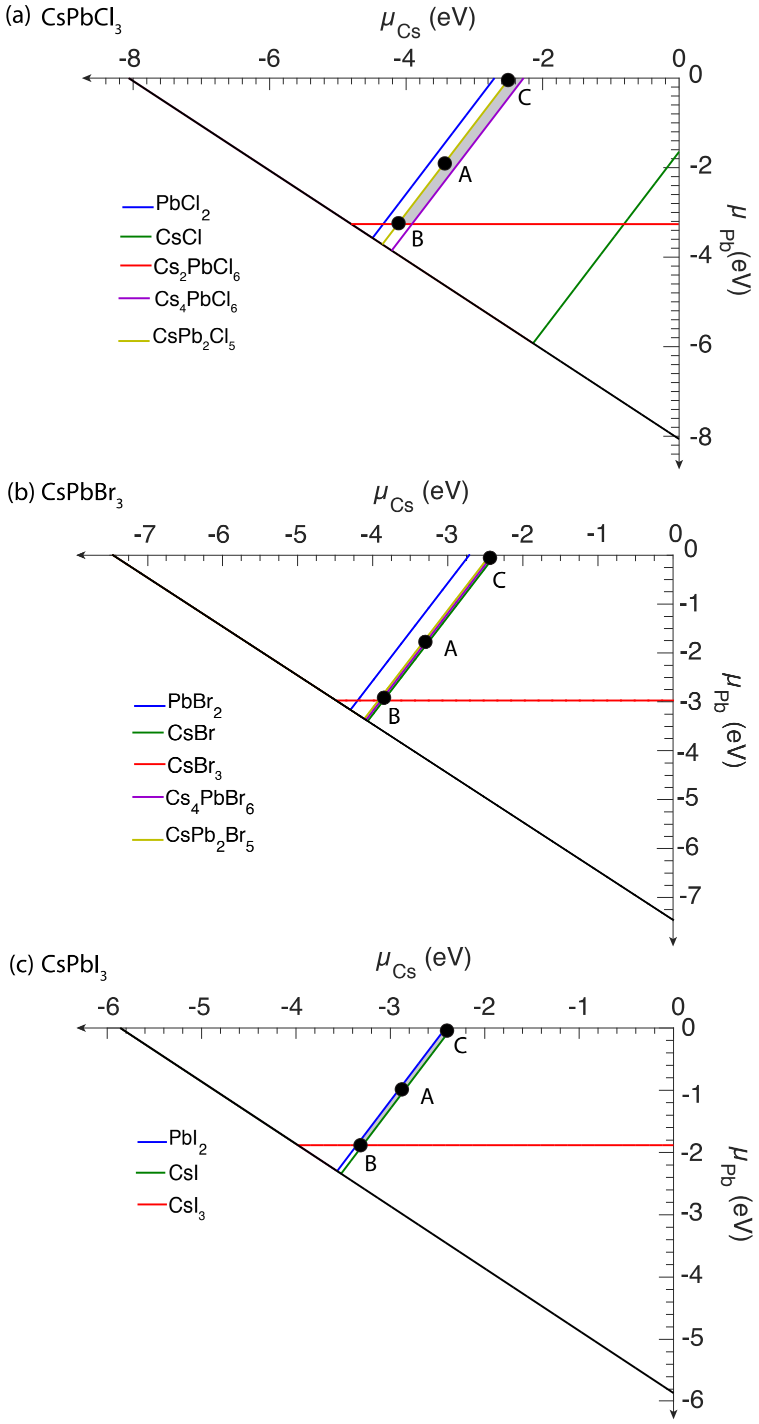


Fig. S4: Full stability triangle for CsPbX$_3$ a) X = Cl, b) X = Br and c) X = I. The stability of the perovskite occurs within the B-C line (shaded region), which represent the closest condition for halogen rich and halogen poor, respectively. Point A represent the intermediate condition and it is determined for one condition that leads to stability of all extrinsic dopants in perovskites analyzed here.

References

1 S. Tao, I. Schmidt, G. Brocks, J. Jiang, I. Tranca, K. Meerholz and S. Olthof, *Nature Communications*, 2019, **10**, 2560.