CRYSTAL CHEMICAL INSIGHTS ON LEAD IODIDE Perovskites Doping FROM REVISED EFFECTIVE RADII OF METAL IONS

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ABSTRACT. Over the last few years of the heyday of hybrid halide perovskites, so many metal cations additives have been tested to improve their optoelectronic properties that it is already difficult to find an element that has not yet been tried. In general, the variety of these approaches is united under the name "doping", however, there is currently no clear understanding of the mechanisms of the influence of the metal ion additives on the properties of the lead halide perovskite materials. For many ions there is even no consensus on the most fundamental questions: what lattice position does a given ion occupy and is it incorporated in the structure at all? Here, we derived a system of effective radii of different metal ions in the iodine environment for the set of iodide compounds and reveal their crystal chemical role in the APbI₃ perovskites. We analysed the possible lattice positions for 40 most common monovalent, divalent, and trivalent metals to reveal whether they could successfully enter into the perovskite structures. We show that, at most, three parameters — effective size, electronegativity and the softness of metal ions are the main ones for crystal chemical analysis of the possibility of metal doping of hybrid halide perovskites. Our results provide a useful theoretical guidance to rationalize and improve current doping strategies of hybrid halide perovskites with metal ions.
**Introduction**

Over the past decade, hybrid halide perovskites (HHPs) have remained on the list of the hottest innovative materials for photovoltaics and optoelectronics due to their unique set of intrinsic properties, such as a direct band gap, strong optical absorption \(^1\), long charge carrier lifetime \(^2,3\) and remarkable tolerance to defects \(^4\). Despite the exceptional progress in the efficiency of solar cells and other perovskite-based devices achieved mainly due to the improvement of existing synthetic methods and optimization of device architectures \(^5\), the potential of these strategies for further boosting the device’s efficiency has been largely exhausted. Therefore, there is a growing demand for approaches to fine-tuning the optoelectronic properties of perovskites, in particular, through doping \(^6,7\).

Importantly, the doping approaches and mechanisms of perovskites differ drastically for hybrid perovskites from those of conventional semiconductors (Si, GaAs) due to the unique chemical and structural origin of the perovskites. Primarily, the nominal doping levels (1-10 mol%) most commonly used for HHPs \(^7-9\) are exceptionally high compared to the conventional semiconductors. Such a high concentration of impurity ions leads potentially to two scenarios: substitution (if possible in terms of the size, electronegativity, and chemical nature of the ion) or the formation of composites containing secondary phases \(^10,11\). The effect of composite formation in a number of cases lead to an improvement in the functional properties of the perovskite layer, but it does not relate to the doping of the material itself, possibility and character of which is the main focus of this article.

Despite the great number of experimental efforts, the rational development of doping approaches for HHPs is hindered by the absence of unambiguous answers on basic questions, concerning the possibility of inclusion of a given ion in the structure as well as its preferable
lattice position. Noteworthy, in most works, the “doped” perovskites were investigated only in terms of the resulting device’s efficiency or by experimental methods with limited sensitivity, such as XRD and XPS providing no unambiguous information about the concentration of the dopant and the mechanism of doping. Unfortunately, reliable experimental techniques on the local structure such as solid-state nuclear magnetic resonance (ss-NMR) were applied only for selected metal ions $^{10-13}$.

In this article, we provide a systematic study of matching of different metal ions to available lattice sites in the structure of three most common halide perovskites: CsPbI$_3$, MAPbI$_3$, and FAPbI$_3$. For this purpose, we calculated and analyzed the effective radii for 40 most common monovalent, divalent, and trivalent metal ions in iodine environment of different compounds valuable as dopants for halide perovskites. The proposed methodology has demonstrated a good agreement with existing experimental data and is proposed to rationalize doping strategies.

**Methods**

**System of ionic radii.** To elucidate appropriate lattice sites for a given ion, a reliable system of ionic radii is required. The direct application of traditional concepts of ionic radii for iodide compounds is fraught with considerable errors due to the larger size and the less electronegativity of iodine compared to oxygen and fluorine for ionic compounds basically used in the concept of Shannon radii and tolerance factors $^{14,15}$. There are two ways to eliminate this inaccuracy: (1) introducing corrections to the reference radius values based on the average M-X bond length $^{16}$ or (2) direct calculation of effective ionic radii from alternative appropriate sets of structural data. The latter can be accurately and facilely calculated as the equivalent radii of spherical domain ($R_{sd}$) of Voronoi-Dirichlet Polyhedra (VDP) derived (see SI), for example, from corresponding space partitioning implemented in the TOPOSPro software package $^{17,18}$.
Being calculated for each ion from a representative set of experimentally refined crystal structures of iodide compounds (including HHPs), the $R_{sd}$-based effective ionic radii, by default, take into account the shortening of the M-I bond for various metals due to a covalent bond contribution. Moreover, $R_{sd}$ for a given atom depends only on the oxidation state, electronic configuration, and the type of neighboring atoms, being approximately constant in different structures and different coordination numbers. Therefore, the single $R_{sd}$ value can be used for different possible lattice sites of a given doping ion (M$^{n+}$) in the crystal structure to elucidate the most appropriate one. In addition, the $R_{sd}$ can be calculated with a high accuracy even for ions with a high degree of polyhedral distortion and irregular coordination, which made it ambiguous to define their ionic radii within traditional hard-sphere models. From this point of view, the effective radii of ions ($R_{sd}$) are more suitable parameter for estimation of effective sizes of doping ions and its possible locations in lead halide perovskites.

**Dopability criterions.** In principle, three possible variants of an insertion of a foreign ion into the ABX$_3$ perovskite structure can be distinguished: the substitution of cations A or B at their own sites, or occupation of an interstitial site. So, comparison of the ionic radius of an impurity ion with the size of a given crystallographic site should be considered as a first discriminating criterion of dopability. The sizes of A and B crystallographic sites in APbI$_3$ lead iodide perovskites were quantitively estimated as the $R_{sd}$ values of A$^+$ and Pb$^{2+}$ cations averaged for different polymorphs (Fig. 2). The $R_{sd}$ values for other ions considered as possible dopants were calculated from a number of corresponding compounds with metal ions in iodine environment from Materials Project database.  

It should be noted that the effective radius of any of the ions depends substantially on the bond ionicity (e.g. $R_{sd}$ of Pb$^{2+}$ decreases significantly in the PbI$_2$-PbBr$_2$-PbCl$_2$-PbF$_2$ series), but is
almost the same in similar environment even despite of the change in the structural type (e.g. from layered PbI$_2$ to perovskite APbI$_3$, see Fig. 2, a). Therefore, we assume that the sizes of ions in the B site can be assumed to be almost the same for all hybrid lead iodide perovskites. At the same time, $R_{sd}$ of a given ion in the same environment has a small scatter even for homologous structures. Typically, this scatter is within ±5% which was chosen as the limiting deviation of the size of the ion occupying a given position (plotted as orange regions on Figures 1-2 and S3-S8 in SI).

In the case of doping via partial Pb substitution in the HHPs structures, an equally important crystal-chemical criterion for the possibility of metal doping is a difference in electronegativity of dopant metal (M) with iodine: $\Delta \chi = \chi(\text{I}) - \chi(\text{M})$. Therefore, the offset of $\Delta \chi$ between Pb and doping metal ($\Delta(\Delta \chi)$) should not exceed the empirical value of 0.4-0.5 eV$^{-1/2}$. In the present study, the $\Delta \chi$ values were calculated based on two electronegativity scales: the Pauling one$^{20}$ and the one recently proposed by Tantardini and Oganov$^{21}$.

The third criterion that takes into account the contribution of the polarizability and ability to be polarized when chemically bound of the cation is softness. Ions with a higher softness usually form stronger complexes with iodide anions, therefore, being in an iodine environment is more energetically favorable for them. Among the many known scales of softness, we have chosen the consensus scale published in$^{22}$ as the most correlated with the experimental properties of ions.
Table 1. Scales of offset in $\Delta \chi$ within Pauling and Tantardini-Oganov scales and softness**.

Green highlight corresponds to $\Delta \chi$ and softness values appropriate for doping via partial Pb substitution.

| Metal ion | $\Delta \chi$ offset in Pauling scale | $\Delta \chi$ offset in Tantardini-Oganov scale | Softness | Metal ion | $\Delta \chi$ offset in Pauling scale | $\Delta \chi$ offset in Tantardini-Oganov scale | Softness |
|-----------|--------------------------------------|-----------------------------------------------|----------|-----------|--------------------------------------|-----------------------------------------------|----------|
| Au$^{+}$  | -0.21                                | 0.19                                          | 1.82     | Ga$^{3+}$ | 0.52                                | 0.19                                          | 0.07     |
| Pt$^{2+}$ | 0.05                                 | -0.36                                         | 1.60     | Zn$^{2+}$ | 0.68                                | 0.36                                          | -0.09    |
| Hg$^{2+}$ | 0.33                                 | -0.3                                          | 1.16     | Mn$^{2+}$ | 0.78                                | 0.42                                          | -0.20    |
| Pd$^{2+}$ | 0.13                                 | -0.08                                         | 1.03     | Lu$^{3+}$ | 1.06                                | -0.06                                         | -0.30    |
| Ag$^{+}$  | 0.4                                  | -0.26                                         | 0.84     | Eu$^{3+}$ | 1.13                                | 0.81                                          | -0.45    |
| Cu$^{+}$  | 0.43                                 | -0.24                                         | 0.65     | Sm$^{3+}$ | 1.16                                | 0.72                                          | -0.45    |
| Bi$^{3+}$ | 0.31                                 | -0.07                                         | 0.58     | Al$^{3+}$ | 0.72                                | 0.1                                           | -0.48    |
| Cu$^{2+}$ | 0.43                                 | -0.24                                         | 0.57     | La$^{3+}$ | 1.23                                | 0.13                                          | -0.53    |
| Pb$^{2+}$ | 0                                    | 0                                             | 0.46     | Rb$^{+}$  | 1.51                                | 0.55                                          | -0.69    |
| Mo$^{3+}$ | 0.17                                 | 0.15                                          | 0.38     | K$^{+}$   | 1.51                                | 0.55                                          | -0.73    |
| Sn$^{2+}$ | 0.37                                 | -0.06                                         | 0.36     | Ba$^{2+}$ | 1.44                                | 0.6                                           | -0.76    |
| Ni$^{2+}$ | 0.42                                 | 0.3                                           | 0.29     | Na$^{+}$  | 1.4                                 | 0.47                                          | -0.80    |
| Ge$^{2+}$ | 0.32                                 | -0.17                                         | 0.27     | Sr$^{2+}$ | 1.38                                | 0.49                                          | -0.88    |
| Co$^{2+}$ | 0.45                                 | 0.28                                          | 0.27     | Be$^{2+}$ | 0.76                                | 0.2                                           | -0.96    |
| In$^{3+}$ | 0.55                                 | 0.33                                          | 0.21     | Li$^{+}$  | 1.35                                | 0.45                                          | -0.97    |
| Cd$^{2+}$ | 0.64                                 | 0.26                                          | 0.17     | Ca$^{2+}$ | 1.33                                | 0.42                                          | -0.99    |
| Fe$^{2+}$ | 0.5                                  | 0.3                                           | 0.14     | Mg$^{2+}$ | 1.02                                | 0.23                                          | -1.02    |

**The consensus scale published in article was chosen as the scale of softness of cations.

Results and discussions

We will consider three types of point defects resulting from foreign metal ion ($M^{n+}$) implementation in APbI$_3$ perovskite structure (electric charges and lattice positions described within Kröger–Vink notation):

1) $M_{A}^{(n-1)+}$ ($M_{A}^{X}$, $M_{A}^{M}$, and $M_{A}^{M'}$ in the case of $n = 1, 2, 3$);

2) $M_{Pb}^{(n-2)+}$ ($M_{Pb}^{Pb}$, $M_{Pb}^{X}$, and $M_{Pb}^{M'}$ in the case of $n = 1, 2, 3$);
3) $M_i^{\text{\textsuperscript{3+}}}$ (for ions in tetrahedral interstitial sites).

**A-site doping**

Due to the large size of cuboctahedral A$^+$ cation site, its doping with a metal ion is, in fact, exclusively represented by the case of substitution with a large monovalent cation (isovalent substitution ($M_A^+$)) since all the divalent metal cations are much smaller. According to the calculated values of $R_{sd}$, among the monovalent cations, only Cs$^+$ has a satisfactory large size to partly substitute the organic MA$^+$ and FA$^+$ cations in the structure (Figure 1a, Figures S3 and S6 in SI). The effective radii of Rb$^+$, K$^+$, and Tl$^+$ are too small to occupy the A site and simultaneously they do not fit to the B site (Figure 1a, Figures S3 and S6 in SI), which indicates that these cations can not be incorporated in the APbI$_3$ structure at all. In the case of admixing of some salts based on these ions into perovskite precursor solution, the latter should lead to separate crystallization of pure perovskite precursor solution, the latter should lead to separate crystallization of pure perovskite phase without “dopants” and with secondary phase(s) containing Rb$^+$, K$^+$, and Tl$^+$ cations. This conclusion fully agrees with experimentally proved by ss-NMR formation of KI and KPbI$_3$ secondary phases for K$^+$ 10 as well as RbPbI$_3$, RbI$_{1-x}$Br$_x$, and Cs$_{0.5}$Rb$_{0.5}$PbI$_3$ ones for Rb$^+$ 11. When non-perovskite wide-bandgap phases of potassium and rubidium are segregated on the grain boundaries 25, they might block an interfacial non-radiative recombination as well as inhibit intralayer diffusion of iodine and organic cations in solar cells, which explains the well-known improvement of optoelectronic properties 26 and suppressed hysteresis 27,28 of resulting film and solar cells respectively.

**B-site doping**

**Monovalent cations.** The two smallest alkali cations in six-fold coordination, Na$^+$ and Li$^+$, have an admissible mean ionic size to occupy the B positions in the structure of perovskites.
However, the large offset in $\Delta \chi$ and in hardness for these cations compared to for Pb$^{2+}$ should prevent them from replacing lead in the APbI$_3$ perovskite. Considering the significant discrepancy in the electronegativity of both the ions according to the both scales used, it can be assumed that their dopability is limited by low concentrations. The possible Na$^{+}$Pb (Li$^{+}$Pb) substitution generates negatively charged defects, which should be compensated by positively charged defects such as iodine vacancies ($V_I^-$) and/or holes (h) (see eqs. in SI). This conclusion agrees well with a large increase of both ionic and electronic conductivity and pronounced p-doping of MAPbI$_3$ perovskite films and single crystals when PbI$_2$ in a precursor solution is partially replaced with NaI$^{29-31}$ and significant upward shift of the Fermi level with LiI additive$^{32}$ (Table S1).

Among the monovalent cations of coinage metals (Cu$^+$, Ag$^+$, Au$^+$), the silver has the most appropriate size, $\Delta \chi$ and softness to be included in the B-site. Since the average $R_{sd}$ of Cu$^+$ and Au$^+$ is only of 10% smaller than that of Pb$^{2+}$ in iodine environment and $\Delta \chi$ is within the limits, a moderate local lattice distortion can also allow them to replace partially lead ions. Similar to sodium, doping of perovskite by these ions should lead to p-type conductivity (if the original material is intrinsic semiconductor). This result is consistent with the decrease in conductivity by one order of magnitude due to the weakening of n-type doping of resulted MAPbI$_3$ perovskite film prepared with the addition of the CuI and AgI salts$^{33}$. Possibilities of other variants of doping are discussed in SI.
**Figure 1.** Calculated $R_{sd}$ of monovalent (a) and divalent (b) metal ions for doping of MAPbI$_3$. The dashed lines show the values of the average $R_{sd}$ of A and B sites in MAPbI$_3$; a possible change in the sizes of A and B sites for isomorphic metal doping is shown in orange.

**Divalent cations.** For the case of doubly charged ions, due to their relatively small size, two doping scenarios can be realized: substitution of lead in B sites or occupation of a four-coordinated interstitial (tetrahedral) positions with corresponding generation of charge balancing defects. An analysis of the diagram in Fig. 2, b shows that Sn$^{2+}$ has the closest size and $\Delta \chi$ to lead in perovskite, predictably forming a continuous series of A${\text{Pb}}_{1-x}{\text{Sn}}_x$I$_3$ solid solution in the entire range of compositions $^{34}$. Divalent mercury is another ion that satisfies all three dopability criterions, having a nearly ideal ionic size, low $\Delta \chi$, and high softness. The solubility limit of Hgl$_2$ in PbI$_2$ having been experimentally determined to be only 600 ppm $^{35}$, which can be explained by the difference in structural types of the two iodides. In the case of MAPbI$_3$, much higher doping limit can be expected from the recent study of Frolova et. al $^{36}$. According to these data, the secondary Hg-rich phases become visible by XRD starting from 20% of Hgl$_2$ and higher only.

On the other hand, there are two large groups of doubly charged cations that definitely cannot replace lead in iodide perovskites. The first of group includes Pt$^{2+}$, Pd$^{2+}$, Mo$^{2+}$, Ni$^{2+}$, V$^{2+}$, Be$^{2+}$, and Mg$^{2+}$ ions, which in similar iodide environment are much smaller than Pb$^{2+}$. Among them, the “soft” cations of d-metals such as Pt$^{2+}$, Pd$^{2+}$, Mo$^{2+}$, which prefer the four-fold iodine coordination and have a relatively small offset of $\Delta \chi$ (and, therefore, the low expected effective charge), may occupy the interstitials if they are complexed with negatively charged defects such as $V_A^{-}$. The second group includes ions of alkaline earth metals (except the Mg$^{2+}$ and Be$^{2+}$) and Eu$^{2+}$; all of them have a large enough size to occupy the octahedral void in the perovskite
structure, however the offset in $\Delta \chi$ is too large, and thus bulk doping at a reasonable level should be excluded. In the absence of suitable positions for incorporation, these ions, apparently, are not capable of doping iodide perovskites. Therefore, additives based on them should be considered exclusively as modifying (passivating) the surface or modulating the crystallization. As for the Ba$^{2+}$, this conclusion is fully corresponds to the EDS-mapping and ss-NMR results indicating respectively the non-uniform distribution and formation of secondary Ba-rich phases for CsPb(I$_{0.66}$Br$_{0.33}$)$_3$ perovskite $^{37}$. Similarly, in the case of Sr$^{2+}$, XPS and XAS spectra clearly indicate a strong enrichment of surface by the dopant and formation of surface phases $^{38}$.

Another set of divalent cations, including Ge$^{2+}$, Co$^{2+}$, Fe$^{2+}$, Cd$^{2+}$, Zn$^{2+}$, and Mn$^{2+}$, is characterized by much more ambiguous doping behavior. All these ions are smaller than lead and have a borderline size. Therefore, to differentiate their role in doping, it is necessary to compare their $\Delta \chi$ and softness. The difference in electronegativities increases in the aforementioned series from left to right, whereas softness increases in the following series Pb$^{2+} >$ Ge$^{2+} >$ Cd$^{2+} \approx$ Co$^{2+} >$ Fe$^{2+} >>$ Zn$^{2+} >$ Mn$^{2+}$ (Table 1), where the first four ions are principally “soft” like lead and the last two ones are relatively “hard”. Based on the two above mentioned criterions, we can assume that Ge$^{2+}$ ions, which are closest to Pb$^{2+}$ in all three parameters, are most likely suitable to substitute the lead in APbI$_3$ perovskites. Interestingly, even the relatively “soft” Cd$^{2+}$ and Co$^{2+}$ cations, as confirmed by ss-NMR, can not be incorporated into the MAPbI$_3$ perovskite structure at doping levels as low as 1 mol % $^{12,13}$. This fact can serve as an evidence of the presence of a rather sharp lower boundary of the limiting size for the ion replacing the B position at a level of about 5% of $R_{sd}$. Accordingly, for Fe$^{2+}$, Zn$^{2+}$, and Mn$^{2+}$ ions, it can be concluded that doping through M$_{Pb}^X$, substitution is hardly possible.
**Trivalent cations.** Among trivalent cations and rare earth elements, the Sb$^{3+}$ and Bi$^{3+}$ are the most suitable in terms of the average effective radius for entering the B site in MAPbI$_3$, FAPbI$_3$ and CsPbI$_3$ (Figure 2, Fig. S5 and S8 in SI) perovskites. It has been shown experimentally that Bi$^{3+}$ and Sb$^{3+}$ can generate M$^+_\text{Pb}$ defects in halide perovskites acting as n-dopants $^{39,40}$. Such defects also generate sub-gap levels in iodide perovskites resulting in significantly red-shifted optical bandgap $^{41}$ and acting as recombination centers lowering the photoluminescence quantum yield $^{42}$.

As for the trivalent cations of 13 group, the In$^{3+}$ have simultaneously average ionic size nearly equal to Pb$^{2+}$, very close value of softness and appropriate $\Delta \chi$. Having a lower electronegativity than lead, In$^{3+}$ is expected to create no sub-gap electronic levels due to higher splitting of $\sigma^*$ and $\pi^*$ orbitals and, therefore, can be considered as a good choice for n-doping of iodide perovskites. In contrast, Ga$^{3+}$, having average $R_{sd}$ outside of $\pm 5\%$ limits and lower softness, is most likely not capable to dope the lead halide perovskites.

The trivalent cations of rare-earth metals (La$^{3+}$, Ce$^{3+}$), likely rare earth cations, have a suitable size to enter the B-sites, but a great offset in the electronegativities and differences in the softness between these cations and Pb$^{2+}$, and that should prohibit the substitution. Therefore, despite the many evidences of control the emission properties of bromide and chloride perovskite nanocrystals $^{43-47}$ by the addition of lanthanide additives, such trick are hardly possible for APbI$_3$ iodide perovskites.
Figure 2. Calculated $R_{sd}$ of trivalent metal ions for doping of MAPbI$_3$. The dashed lines show the values of the average $R_{sd}$ of A and B sites in MAPbI$_3$.

Table 2. Appropriate lattice sites for dopability cations and their expected effect on electronic properties based on equations of point defects formation (see SI).

| Lattice site        | Ions                              | Expected effect on electronic properties                                                                 |
|---------------------|-----------------------------------|-----------------------------------------------------------------------------------------------------------|
| A-site              | Cs$^+$, Rb$^+$                    | Structure (de)stabilization                                                                             |
| B-site              | Ag$^+$, Cu$^+$, Au$^+$ (CN = 6), Na$^+$, Li$^+$ | p-type conductivity                                                                                   |
|                     | Sn$^{2+}$, Ge$^{2+}$, Hg$^{2+}$    | Change in band structure, lowering bandgap                                                               |
|                     | In$^{3+}$, Sb$^{3+}$*, Bi$^{3+}$*  | n-type doping; *sub-gap levels                                                                           |
| Tetrahedral         | Ag$^+$, Cu$^+$, Au$^+$ (CN = 4)   | Strong n-type doping and increased ionic conductivity due to the migration of foreign cation            |
| interstitial**      | Pt$^{2+}$, Pd$^{2+}$, Mo$^{2+}$, Ni$^{2+}$ |                                                                                                           |
| No appropriate      | K$^+$, Tl$^+$, alkaline earth, rare earth (M$^{3+}$), divalent and | Surface passivation / Surface doping                                                                     |
| site                |                                   |                                                                                                           |
trivalent d-metal ions***

**may exist in complex with negatively charged defects such as \( V_A^- \) or \( I_A^- \)

*** excluded the abovementioned

The discussed considerations regarding possible dopants and their influence on the optoelectronic properties of MAPbI\(_3\) are summarized in the Table 2. It should be noticed that there are obvious differences in the dopability of MA-, FA-, and Cs-based perovskites by the same ion, caused by the difference in the size of A and B lattice sites in their structures (see Figures 1-2 and Figures S3-S8). Especially, the increased \( R_{sd}(\text{Pb}^{2+}) \) for FAPbI\(_3\) in comparison with MAPbI\(_3\) makes the substitution of M\(_{\text{Pb}}\) type more unlikely for ions close to the lower limit of the admissible effective radius, such as Cu\(^+\), Ag\(^+\), Au\(^+\), and Li\(^+\).

**The effect of the point defects on the doping.** All the above mentioned results are based on an assumption that the halide perovskites have perfect structure before doping. However, both the defect tolerance and soft nature of halide perovskites\(^ {48} \), partly aggravated by the domination of solution processing methods, often lead to the formation of various point defects at relatively high concentrations\(^ {6,49} \). The requirement of bulk charge neutrality assume that there are two classic types of defects in halide perovskites: the Schottky defects (\( X \Leftrightarrow V_I^- + V_{MA}^+ + MA_{surf} + I_{surf} \)) and anionic Frenkel pairs (\( I_I^X \Leftrightarrow V_I^+ + I_I^- \)). The presence of Schottky bivacancies may facilitate the incorporation of almost any metal ion or ionic associates due to their large size. It worth to note that the formation of interstitial iodide as a stable defect in these perovskite is hardly possible due to geometric considerations (\( R_{sd}(\text{I}) >> R_{sd}(i) \)), therefore, the iodide anions occupying the interstitials should be ionized. Accordingly, one should also consider an influence of such defects on the doping process.
We expect that the presence of \( V_i^+ \) (e.g. after a prolonged annealing or in case of PbI\(_2\) excess\(^{50,51}\)) should increase the available sizes of \( R_{sd}(A) \) and \( R_{sd}(B) \). It facilitates the doping by the metal ions with \( R_{sd} \) larger than \( R_{sd}(\text{Pb}^{2+}) \) especially in the case of heterovalent doping with \( M^{3+} \) cations to the B position, associated with \( I_i^+ \) formation as shown by the equation 1:

A defect-free case:
\[
\text{Pb}^\infty_{\text{Pb}} + \text{MI}_3 = M^*_\text{Pb} + I_i' + \text{PbI}_2 \Leftrightarrow M^*_\text{Pb} + I_i^+ + e^- + \text{PbI}_2 \Leftrightarrow M^*_\text{Pb} + e^- + \text{PbI}_2 + \frac{1}{2}\text{I}_2
\]  
(Eq. 1)

A defect-influenced case:
\[
\text{Pb}^\infty_{\text{Pb}} + V_i^+ + \text{MI}_3 = M^*_\text{Pb} + I_i' + V_i^+ + \text{PbI}_2 \Leftrightarrow M^*_\text{Pb} + \text{PbI}_2
\]  
(Eq. 2)

This scenario seems to be possible for lanthanides cations and could explain the existence of Eu-doping used for well-known Eu\(^{3+}\)-Eu\(^{2+}\) ion redox shuttle proposed to improve the stability of perovskite solar cells\(^{52}\).

In contrast, the presence of \( I_i' \) (e.g. formed during the photodegradation of the perovskite\(^{53}\)) decreases the size of \( R_{sd} \) of neighboring A and B positions and, therefore, facilitates the incorporation to the B position of cations with \( R_{sd} \) smaller than \( R_{sd}(\text{Pb}^{2+}) \). In the case of \( M^+ \) cations the additional driving force would be provided by the shift of an equilibrium of the defect formation associated with the formation of \( V_i^+ \):

A defect-free case:
\[
I_i^+ + \text{Pb}^\infty_{\text{Pb}} + \text{MI} = M^*_\text{Pb} + V_i^+ + \text{PbI}_2
\]  
(Eq. 3)

A defect-influenced case:
\[
I_i^+ + \text{Pb}^\infty_{\text{Pb}} + I_i' + \text{MI} = M^*_\text{Pb} + V_i^+ + I_i' + \text{PbI}_2 \Leftrightarrow M^*_\text{Pb} + \text{PbI}_2
\]  
(Eq. 4)

This scenario could be realized in the case of Li\(^+\) ions, migrating from Li-doped Spiro-MeOTAD hole transporting layer to perovskite layer upon solar cell operation\(^{53,54}\).
Conclusions

To sum up, we found that the most important parameters affecting the doping of lead iodide perovskites are the effective sizes ($R_{sd}$) of doping metal ions, their difference in electronegativity ($\Delta \chi$) and the softness. To calculate the effective sides of metal ions we introduce new scale of ionic radii based on $R_{sd}$ parameters calculated from the set of structures containing these ions in iodine environment. Using the proposed approach, we show that among monovalent alkali metal cations, Cs$^+$ and Rb$^+$ are suitable to occupy the A-site, while K$^+$ should form secondary phases and passivate the grain boundaries. The Cu$^+$, Ag$^+$, Au$^+$, Na$^+$ and Li$^+$ can occupy B-site and cause the p-doping of HHPs. The most suitable divalent cations for doping with entering in the B site are Sn$^{2+}$ and Hg$^{2+}$. Among the trivalent cations, Sb$^{3+}$, In$^{3+}$, and Bi$^{3+}$ are the most suitable to occupy the B-site and to induce the n-doping of HHPs. Ag$^+$, Cu$^+$, Au$^+$ (CN = 4), Pt$^{2+}$, Pd$^{2+}$, Mo$^{2+}$, and Ni$^{2+}$ can localize in tetrahedral interstitial positions as also associated with negatively charged defects, leading to n-type doping and increased ionic conductivity due to the migration of foreign cation. Finally, our results provide a guidance for improving current doping engineering strategies of lead iodide perovskites by metal ions.

ASSOCIATED CONTENT

The supporting information file contains technical details of Voronoi-Dirichlet Polyhedra approach, scales of offset in $\Delta \chi$ and softness, quasi chemical equations of possible doping scenarios for monovalent, divalent and trivalent cations, comparison of calculated $R_{sd}$ of monovalent, divalent and trivalent metal ions with sizes of A- and B-site in FAPbI$_3$ and CsPbI$_3$ perovskites, doping of hybrid perovskites by metal ions and their effect on electronic properties according to literature data.
AUTHOR INFORMATION

Notes
The authors declare no competing financial interests.

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CRYSTAL CHEMICAL INSIGHTS ON LEAD IODIDE PEROVSKITES DOPING FROM REVISED EFFECTIVE RADII OF METAL IONS

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SUPPORTING INFORMATION
**Voronoi-Dirichlet Polyhedra approach**

Effective atomic size in crystal structure correlates with geometrical parameters of atomic VDP: a convex polyhedron whose faces are perpendicular to segments connecting the central atom of VDP and other atoms. In the general case, the coordination polyhedron of an ion in crystal structure is dual to the VDP (Figure S1). The VDP characterize either relative, or the absolute atomic size in crystal structure [1].

**Figure S1.** a) Coordination polyhedron (cuboctahedron) of Cs in a cubic CsPbI$_3$ perovskite and its dual VDP (rhombododecahedron); VDP for lead (left), iodine (right) in a tetragonal MAPbI$_3$ structure.
**Figure S2.** The effective radii ($R_{sd}$) of (a) Pb$^{2+}$ and (b) A$^+$ cations in different crystal structures.

Comparison of calculated values of $R_{sd}$ by the Voronoi-Dirichlet partition and the Hirschfeld method for Cs$^+$, Pb$^{2+}$ and I$^-$ in different crystal structures is shown in the Figures S9-S11.

**Possible doping scenarios for monovalent, divalent and trivalent cations**

The following are the main doping scenarios that are possible in the cases of occupation of position A by a single-charged (1), double-charged (2), and triple-charged (3) cation; occupation of position B by a single-charged (4), double-charged (5), and triple-charged (6) cation, as well as occupation of tetrahedral interstitial positions ($i_t$) by single-charged (7), double-charged (8), and triple-charged (9) cations. For each of the doping equations, possible equilibria leading to generation of charge carriers (free electrons $e^-$ and holes $h^+$) through the ionization of formed defects or the removal of components are given.

Also, each of the equations is combined with equation (0) of the self-doping of perovskite due to the formation of the most common anti-Frenkel defects.

0) $I_i^x \Leftrightarrow V_i^x + I_i^x \Leftrightarrow V_i^x + I_i^x + e^-$  \hspace{1cm} (Eq. 0)

Hereinafter, we assume that the formation of interstitial iodide as a stable defect is hardly possible due to geometric considerations ($R_{sd}(\Gamma) \gg R_{sd}(i_t)$); therefore, the iodide anions occupying the interstitials should be ionized.

1) $M^+ \rightarrow A$

$0 + MI = M_A^+ + AI$  \hspace{1cm} (Eq. 1)

Scenario is possible for following ions: Cs$^+$. Result: no effect on type of conductivity, no traps.

2) $M^{2+} \rightarrow A$

$0 + MI_2 = M_A^+ + I_i^x + AI \Leftrightarrow M_A^+ + I_i^x + e^- + AI \Leftrightarrow M_A^+ + e^- + AI + \frac{1}{2}I_2$  \hspace{1cm} (Eq. 2)
Scenario is possible for following ions: $\varnothing$ (no double-charged metal ions with size enough to occupy the A site are known)

Result: n-doping

3) $M^{3+} \rightarrow A$

$$0 + MI_3 = M_A^{*} + 2I'_1 + Al \Leftrightarrow M_A^{*} + 2I^x_1 + e^- + Al \Leftrightarrow M_A^{*} + e^- + Al + I_2$$  \hspace{1cm} (Eq. 3)

Scenario is possible for following ions: $\varnothing$

Result: n-doping

4) $M^+ \rightarrow B$

$$I_1^x + \text{Pb}_{Pb}^x + MI = M_{Pb}^{'} + V'_1 + \text{PbI}_2$$  \hspace{1cm} (Eq. 4.1)

$$0 + MI + Al = M_{Pb}^{'} + A_{A}^x + 2I_1^x + V'_1$$  \hspace{1cm} (Eq. 4.2)

$$\{V'_1 + I_1^x + e^-\} + \text{Pb}_{Pb}^x + MI \Leftrightarrow M_{Pb}^{'} + V'_1 + \text{PbI}_2$$  \hspace{1cm} (Eq. 4.3)

$$\{V'_1 + I_1^x + e^-\} + MI + Al = M_{Pb}^{'} + A_{A}^x + 3I_1^x + h^+$$  \hspace{1cm} (Eq. 4.4)

Scenario is possible for following ions: Cu$^+$, Ag$^+$, Au$^+$, Na$^+$, and Li$^+$ (if CN = 6).

Result: “dedoping” of initially n-doped perovskite, increase of ionic conductivity (due to increase of $V'_1$ concentration) or p-doping in the case of [Pb$^{2+}$/M$^+$] stoichiometric replacement in solution; traps formation is possible if the ion can change the oxidation state (Cu$^+$, Ag$^+$, Au$^+$).

5) $M^{2+} \rightarrow B$


\[ \text{Pb}_\text{Pb}^x + \text{M}_2 = \text{M}_\text{Pb}^x + \text{PbI}_2 \]  
(Eq. 5.1)

\[ 0 + \text{AI} + \text{M}_2 = M_{\text{Pb}}^x + A_{\text{A}}^x + 3I_i^x \]  
(Eq. 5.2)

Scenario is possible for following ions: Sn\(^{2+}\), Hg\(^{2+}\), Ge\(^{2+}\).

Result: no-doping, trap formation (especially, change of the oxidation state of Sn\(^{2+}\) and Ge\(^{2+}\)).

6) \( M^{3+} \rightarrow B \)

\[ \text{Pb}_{\text{Pb}}^x + \text{M}_3 = M_{\text{Pb}}^x + I_i' + \text{PbI}_2 \Leftrightarrow M_{\text{Pb}}^* + I_i^x + e^- + \text{PbI}_2 \Leftrightarrow M_{\text{Pb}}^* + e^- + \text{PbI}_2 + \frac{1}{2}I_2 \]  
(Eq. 6.1)

\[ 0 + \text{AI} + \text{M}_3 = M_{\text{Pb}}^x + A_{\text{A}}^x + 3I_i^x + I_i' \Leftrightarrow M_{\text{Pb}}^* + A_{\text{A}}^x + 3I_i^x + I_i^x + e^- \Leftrightarrow M_{\text{Pb}}^* + A_{\text{A}}^x + 3I_i^x + e^- + \frac{1}{2}I_2 \]  
(Eq. 6.2)

Scenario is possible for following ions: Bi\(^{3+}\), Sb\(^{3+}\), In\(^{3+}\).

Result: n-doping, trap formation for Bi\(^{3+}\), Sb\(^{3+}\).

7) \( M^+ \rightarrow i_i \)

\[ 0 + \text{MI} = M_i^* + I_i' \Leftrightarrow M_i^* + I_i^x + e^- \Leftrightarrow M_i^* + e^- + \frac{1}{2}I_2 \]  
(Eq. 7.1)

\[ 0 + A_{\text{A}}^x + \text{MI} = M_i^* + V_{\text{A}}^* + \text{AI} \]  
(Eq. 7.2)

Scenario is possible for following ions: Cu\(^+\), Ag\(^+\), Au\(^+\), and Li\(^+\) (if CN = 4).

Result: n-doping, traps formation.

8) \( M^{2+} \rightarrow i_i \)

\[ 0 + \text{MI}_2 = M_i^* + 2I_i' \Leftrightarrow M_i^* + 2I_i^x + e^- \Leftrightarrow M_i^* + e^- + I_2 \]  
(Eq. 8.1)
Scenario is possible for following ions: Pt$^{2+}$, Pd$^{2+}$, Mo$^{2+}$, and Ni$^{2+}$ (if CN = 4).

Result: n-doping, traps formation is possible if the ion can change the oxidation.

9) M$^{3+}$ → $i_t$

\[ 0 + MI_3 = M_i^{***} + 3I_i' \Leftrightarrow M_i^{***} + 3I_i^X + e^- \Leftrightarrow M_i^{***} + e^- + \frac{3}{2}I_2 \]  

(Eq. 9.1)

\[ 0 + A_A^x + MI_3 = M_i^{***} + 2I_i' + V_A' + Al \Leftrightarrow M_i^{***} + A_i'' + I_i^X + Al \Leftrightarrow M_i^{***} + A_i'' + e^- + Al + \frac{1}{2}I_2 \] 

(Eq. 9.2)
Comparison of calculated $R_{sd}$ of monovalent, divalent and trivalent metal ions with sizes of A- and B-site in FAPbI$_3$ and CsPbI$_3$ perovskites

**Figure S3.** Calculated $R_{sd}$ of monovalent metal ions for doping FAPbI$_3$. The dashed lines show the values of the average $R_{sd}$ of A and B sites in FAPbI$_3$. 
Figure S4. Calculated $R_{sd}$ of divalent metal ions for doping FAPbI$_3$. The dashed lines show the values of the average $R_{sd}$ of A and B sites in FAPbI$_3$. 
Figure S5. Calculated $R_{sd}$ of trivalent metal ions for doping FAPbI$_3$. The dashed lines show the values of the average $R_{sd}$ of A and B sites in FAPbI$_3$.

![Graph showing $R_{sd}$ values for FAPbI$_3$](image)

Figure S6. Calculated $R_{sd}$ of monovalent metal ions for doping CsPbI$_3$. The dashed lines show the values of the average $R_{sd}$ of A and B sites in CsPbI$_3$.

![Graph showing $R_{sd}$ values for CsPbI$_3$](image)
Figure S7. Calculated $R_{sd}$ of divalent metal ions for doping CsPbI$_3$. The dashed lines show the values of the average $R_{sd}$ of A and B sites in CsPbI$_3$. 
**Figure S8.** Calculated $R_{sd}$ of trivalent metal ions for doping CsPbI$_3$. The dashed lines show the values of the average $R_{sd}$ of A and B sites in CsPbI$_3$.

**Figure S9.** Calculated values of $R_{sd}$ by the Voronoi-Dirichlet partition and the Hirschfeld method for Cs$^+$ in different crystal structures.

**Figure S10.** Calculated values of $R_{sd}$ by the Voronoi-Dirichlet partition and the Hirschfeld method for Pb$^{2+}$ in different crystal structures.
Figure S11. Calculated values of \( R_{sd} \) by the Voronoi-Dirichlet partition and the Hirschfeld method for I in different crystal structures.
Table S1. Doping of hybrid perovskites by metal ions and their effect on electronic properties according to literature data.

| Ion added to precursors | Methods | Perovskite | Result | Refs |
|------------------------|---------|------------|--------|------|
| Li⁺                    | PL, TRPL, UPS | MAPbI₃ | Work function downshift from 4.2 eV to 3.76 eV (10%); enhanced PL intensity and prolonged PL lifetime | [6] |
| Na⁺                    | HAADF STEM el. mapping | MAPbI₃ | Formation of Na-rich phases mostly at the grain boundaries & interfaces of the perovskite film | [7] |
| Na⁺                    | PL, TPV, SIMS | MAPbI₃ | Enhance in PL and charge carrier lifetime for films on PTAA. Possibility of Na-doping from soda-lime glass. | [8] |
| K⁺                     | ss-NMR | | Formation of secondary phases: KI, KPB₁₃, Cs₀.₅K₀.₅PbI₃; no doping | [9] |
| K⁺                     | ss-NMR | | Formation of secondary phases: KI, KPbI₃, Cs₁₋ₓKₓPbI₃; no doping | [10] |
| Rb⁺                    | ss-NMR | | Formation of secondary phases: RbPbI₃, RbI₁₋ₓBrₓ, δ-Cs₁₋ₓRbₓPbI₃; no doping | [10] |
| Cs⁺                    | ss-NMR | | Doping - Csₓ⁺; solid solutions: CsₓFA₁₋ₓPbI₃, CsₓMA₁₋ₓPbI₃, CsₓFA₁₋ₓPb(1₋ₓBrₓ)₃54 | [10] |
| Cu⁺                    | HAADF STEM el. mapping, SCLC | MAPbI₃ | Drop in conductivity by an order of magnitude, uniform distribution | [7] |
| Ag⁺                    | HAADF STEM el. mapping, SCLC | MAPbI₃ | Formation of Ag-rich inclusions in perovskite; Drop in conductivity by an order of magnitude | [7] |
| Ag⁺                    | PL, UV-Vis spectroscopy | CsPbI₃ (QDs), x = 1-9% | Blue shift of PL maximum < 8 nm, Suppression of band tail states in abs. spectra | [11] |
| Ag⁺                    | UPS, XPS, PL, TRPL | MAPbI₃ | Downward shift of the Fermi level and reduced electron concentration, no shift of PL, increased carrier lifetime (TRPL) | [12] |
| Ion | Technique | Material | Comment |
|-----|------------|----------|---------|
| Mg$^{2+}$ | HAXPES* | MAPbI$_3$ | Phase segregation at C(Mg$^{2+}$) > 1 %  
More n-type at (Ca$^{2+}$)<2 %, less n-type at (Ca$^{2+}$) > 2 % |
| Ca$^{2+}$ | HAXPES* | MAPbI$_3$ | Phase segregation at C(Ca$^{2+}$) > 0.5 % |
| Sr$^{2+}$ | HAXPES* | MAPbI$_3$ | Phase segregation at C(Ca$^{2+}$) > 0.2 %  
More n-type at (Ca$^{2+}$)<0.5 %, less n-type at (Ca$^{2+}$)>0.5 % |
| Ba$^{2+}$ | ss-NMR, EDS-mapping | CsPbI$_2$Br | Ba/Pb = 0 – 40%: impurity barium-rich non-perovskite phases formation, non-uniform element distribution |
| Mn$^{2+}$ | ss-NMR | CsPbBr$_3$, CsPbCl$_3$ | Incorporation in structure (up to at least 8mol% and 3% for CsPbBr$_3$ and CsPbCl$_3$) |
| Co$^{2+}$ | ss-NMR | MAPbI$_3$ | No doping (formation of cobalt-rich phases with) |
| Eu$^{2+}$ | ss-NMR, HAADF STEM el. mapping | CsPbI$_2$Br | Europium is incorporated into perovskite structure and uniformity distributed inside the perovskite grains. |
| Ge$^{2+}$ | XRD, PL | CsPbI$_2$Br | Incorporation up to 20% (based on XRD data) |

*Films were annealed at 280 °C for 10 min in dry air box;

EDS – ; HAADF STEM – high-angle annular dark-field scanning transmission electron microscopy. STEM-EDX elemental analysis

PCE increase: [7] (from 16.5 to 19-20 for Na, Ag, Cu),

In the recent study it was suggested based on microstrain analysis from GIXRD data that magnesium and strontium can be incorporated into perovskite structure in form of Mg$_{8Pb}$ and
Sr$_x$Pb with maximum concentration of 1% and 0.2% respectively [13]. However, the results of hard x-ray photoelectron spectroscopy (HAXPES) suggests that no doping bulk occurs but surface doping is possible.

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