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Theoretical assessment of metal ions doping of hybrid lead bromide perovskites

Ekaterina I. Marchenko,[a,b] Sergey A. Fateev,[a] Li Yumao,[a,c] Nikolay N. Eremin,[b] Eugene A. Goodilin[a,d] and Alexey B. Tarasov*[a,d]

[a] *Department of Materials Science, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation. E-mail: alexey.bor.tarasov@yandex.ru*
[b] *Department of Geology, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation*
[c] *Faculty of Materials Science, Shenzhen MSU-BIT University, Longgang District, 518572 Shenzhen, China*
[d] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation*

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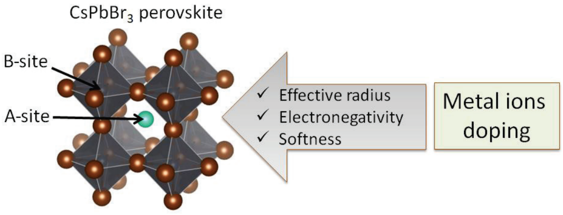
A new system of effective radii of metal ions in the bromide environment has been developed to analyze the dopability and preferable lattice positions for 40 different cations in the structure of wide-gap bromide perovskites with a huge potential for applications in optoelectronics, depending on the appropriate doping. The analysis carried out provides theoretical guidance on rational doping from a crystal chemistry point of view and highlights clear differences compared to well-known lead iodide perovskites.



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Over the past decade, lead halide perovskites (LHPs) have become one of the most studied materials for optoelectronics and photovoltaics due to their unique properties such as direct band gap, strong optical absorption,[1] long charge carrier lifetime[2,3] and tolerance to defects.[4]

Strategies for selective doping of LHPs with metal ions are used to tune the optoelectronic properties of these materials.[5,6] Despite a large number of experimental efforts, further rational development of approaches to doping LHPs is hampered by the lack of unambiguous answers to fundamental questions concerning the possibility of including an ion in the structure (dopability), its preferable lattice position and the structural or physical consequences of such doping. Recently, we developed a new crystal chemical approach to rationalize the strategy of doping lead iodide perovskites $APbI_3$ with methylammonium (MA^+), formamidinium (FA^+) or cesium cations.[7] Here, we have provided a crystal chemical insight into the doping of hybrid lead bromide perovskites $APbBr_3$ ($A = MA^+$, FA^+ or Cs^+) with mono-, di- and trivalent metal ions based on three main criteria, namely, electronegativity, effective radii and ion softness.

To analyze the dopability of $APbBr_3$ perovskites with metal ions, we used three crystal chemical criteria: (1) effective radii in the bromide environment, (2) difference in electronegativity and (3) ion softness. For each ion, the effective radius was calculated as the equivalent radius of the spherical domain (R_{sd}) of the Voronoi−Dirichlet polyhedron[8] from a representative set of experimentally refined crystal structures of bromide compounds containing this ion completely surrounded by bromide ions in the first coordination sphere.[†] The difference in the electronegativity of a given metal with respect to Pb ($\Delta\chi = \chi_{Pb} - \chi_M$) was chosen as the second criterion of dopability in the case of incorporation of ions into Pb lattice positions. According to the Goldsmith rule, we assumed that doping is possible if the value of $\Delta\chi^{‡}$ is less than the empirical value of 0.4−0.5 $eV^{-1/2}$. The softness of the ions was taken from the known work,[12] since it correlates well with the experimentally known properties of the ions.

Comparison of the calculated effective radii R_{sd} of metal ions with the R_{sd} values of sites in the structures of $APbBr_3$ halide perovskites makes it possible to consider three appropriate lattice sites for the incorporation of foreign ions: A-site (with the substitution for A^+ cations in the structure), B-site (with the substitution for Pb^{2+} ions) and a tetrahedral interstitial (presumably with the formation of a complex with negatively charged defects, a detailed quasi-chemical description of which has recently been published).[7] Further, we consistently consider the possible types of doping with monovalent (Figure 1), divalent (Figure 2) and trivalent (Figure 3) ions.

Among monovalent cations, only Cs^+ has a suitable effective radius to partly substitute for the organic MA^+ and FA^+ cations in A-sites in perovskite structures, whereas the Au^+, Ag^+, Cu^+, Tl^+, Li^+ and Na^+ ions can occupy B-sites according to the scheme of heterovalent substitution. However, the large offset in $\Delta\chi$ (on the Pauling scale) and hardness for the Tl^+, Li^+ and Na^+ cations as compared to these values for Pb^{2+} should prevent them from replacing lead in $APbBr_3$ perovskites. Considering the significant discrepancy between the electronegativity of these ions on the Pauling scale, it can be assumed that their dopability is limited to low concentrations. The effective radii of Rb^+ and K^+ are either

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[†] We adopted this methodology from our recent publication[7] and used the TOPOSPro software package for the assessment.[9]

[‡] The values were calculated using two electronegativity scales (the Pauling scale[10] and the Tantardini–Oganov scale[11]).

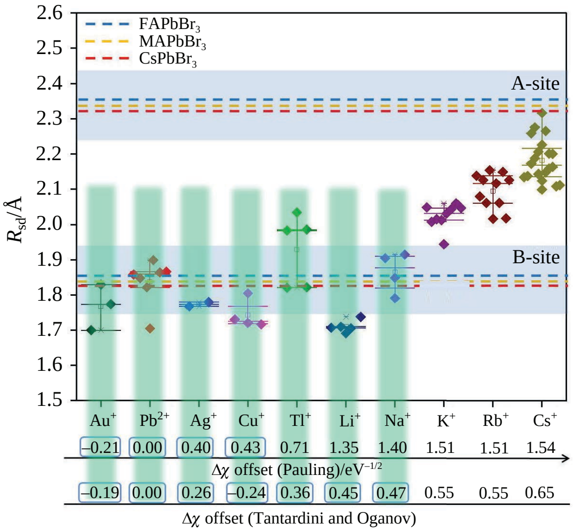

Figure 1 Calculated R_{sd} values of monovalent metal ions considered for doping of APbBr$_3$ perovskites. Dashed lines show the average R_{sd} values of A- and B-sites in MAPbBr$_3$, FAPbBr$_3$ and CsPbBr$_3$. Squares represent the radii of metal ions in an iodide environment for different crystal structures.

too small or too large to occupy sites A and B, respectively (hence why they are not highlighted in green in Figure 1). However, partial substitution of Cs$^+$ for Rb$^+$ helps to stabilize the orthorhombic perovskite-like phase of RbPbBr$_3$ in the form of nanocrystals.[13]

Among divalent cations, two doping scenarios can occur: the substitution for the Pb^{2+} ion in B-sites or the occupation of four-coordinated positions (tetrahedral voids) with the corresponding generation of charge-balancing defects. Analysis of the diagram in Figure 2 confirms that the Hg^{2+} and Sn^{2+} ions meet all dopability criteria, having an almost ideal ionic size, a small Δχ value and high softness. However, the diagram in Figure 2 also shows that divalent cations such as Co^{2+}, Cd^{2+} and Zn^{2+},[14] with slightly smaller radii than the lead ion, are also appropriate for B-sites in the bromide environment, having suitable Δχ values (on the Tantardini–Oganov scale).

The Pt^{2+}, Pd^{2+}, Ni^{2+}, V^{2+}, Be^{2+} and Mg^{2+} ions are smaller than the Pb^{2+} ion in the bromide environment, and therefore can occupy the tetrahedral interstices if they form complexes with negatively charged defects, such as cation vacancies in the A-sites.[7] However, a large difference in Δχ and the crystal field stabilization energy limit the incorporation of Ni^{2+}, Be^{2+} and Mg^{2+} ions. All alkaline-earth metal ions (except Mg^{2+} and Be^{2+}) and the Eu^{2+} ion are large enough to occupy the octahedral voids in the perovskite structure, but the difference in Δχ 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 lead bromide perovskites. Therefore, if added to the precursors of LHPs synthesis, these ions are expected to form secondary phases, as found experimentally, for example, for the Ba^{2+} ion.[15]

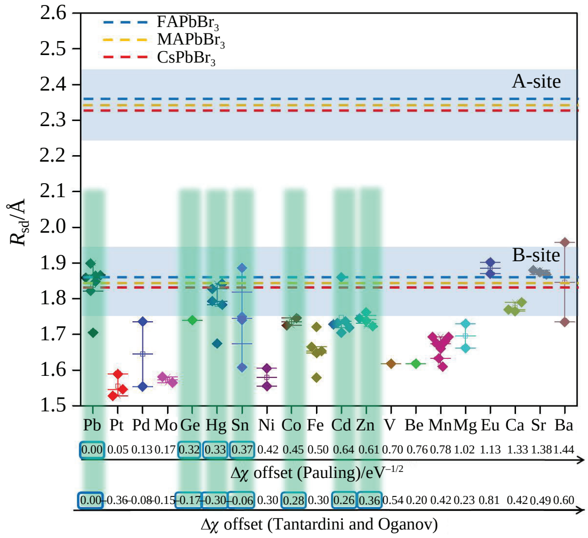

Figure 2 Calculated R_{sd} values of divalent metal ions considered for doping of APbBr$_3$ perovskites. Dashed lines show the average R_{sd} values of A- and B-sites in MAPbBr$_3$, FAPbBr$_3$ and CsPbBr$_3$. Squares represent the radii of metal ions in an iodide environment for different crystal structures.

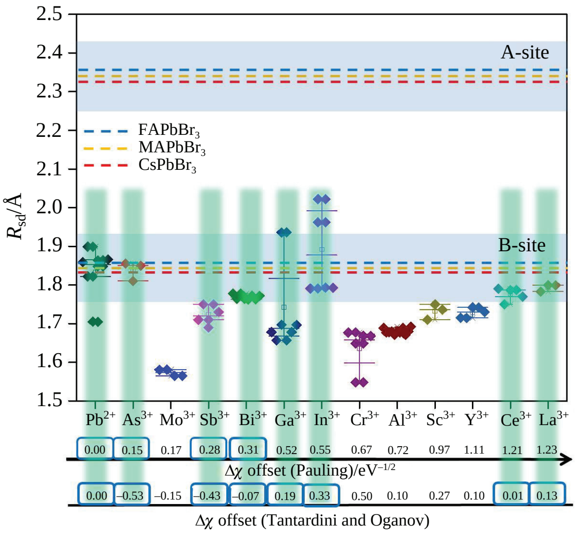

Figure 3 Calculated R_{sd} values of trivalent metal ions considered for doping of APbBr$_3$ perovskites. Dashed lines show the average R_{sd} values of A- and B-sites in MAPbBr$_3$, FAPbBr$_3$ and CsPbBr$_3$. Squares represent the radii of metal ions in an iodide environment for different crystal structures.

Among trivalent cations, including rare-earth elements, As^{3+}, Sb^{3+} and Bi^{3+} ions (on the Pauling electronegativity scale) and As^{3+}, Sb^{3+}, Bi^{3+}, Ga^{3+}, In^{3+}, Ce^{3+} and La^{3+} ions (on the Tantardini–Oganov electronegativity scale) are the most suitable in terms of the average effective radius to enter B-sites in APbBr$_3$ perovskites. In addition, there is a lot of experimental evidence for controlling the emission properties of bromide and chloride perovskite nanocrystals with the help of lanthanide additives.[16–20] The Cr^{3+} and Al^{3+} ions have much smaller radii than lead in APbBr$_3$. Therefore, the occupation of B-sites in APbBr$_3$ perovskites with these metal ions will be difficult.

In summary, we calculated the effective radii of mono-, di- and trivalent metal ions in the bromide environment and revealed their crystal chemical role in perovskites APbBr$_3$ (A = MA$^+$, FA$^+$ or Cs$^+$) using three dopability criteria: effective radius, electronegativity and softness. Using the proposed approach, we have shown that lead bromide perovskites can be doped with a greater variety of metal ions than lead iodide perovskites. This difference is due to the fact that the ionic radius of the bromide ion is smaller than that of the iodide. Although A-sites in bromide perovskites can be occupied only by Cs$^+$ ions, as in iodide perovskites, other monovalent cations (Au$^+$, Cu$^+$, Ag$^+$, Tl$^+$, Na$^+$ and Li$^+$) can occupy B-sites according to the scheme of heterovalent substitution . The most suitable divalent cations for B-site doping are Sn^{2+}, Hg^{2+}, Co^{2+}, Cd^{2+} and Zn^{2+}. Among the trivalent cations, As^{3+}, Sb^{3+}, In^{3+}, Bi^{3+}, Ga^{3+}, Ce^{3+} and La^{3+} are the most suitable for occupying B-sites according to the scheme of heterovalent substitution, which can be beneficial for tuning the optical properties of lead bromide perovskites. We hope that our results will be useful for a targeted metal doping strategy for hybrid lead halide perovskites to improve their optoelectronic characteristics.

References

1 S. De Wolf, J. Holovsky, S.-J. Moon, P. Löper, B. Niesen, M. Ledinsky, F.-J. Haug, J.-H. Yum and C. Ballif, *J. Phys. Chem. Lett.*, 2014, **5**, 1035.

2 A. A. Zhumekenov, M. I. Saidaminov, M. A. Haque, E. Alarousu, S. P. Sarmah, B. Murali, I. Dursun, X.-H. Miao, A. L. Abdelhady, T. Wu, O. F. Mohammed and O. M. Bakr, *ACS Energy Lett.*, 2016, **1**, 32.

3 A. A. Zhumekenov, M. I. Saidaminov and O. M. Bakr, in *World Scientific Handbook of Organic Optoelectronic Devices*, eds. F. So, J. Huang and B. C. Thompson, World Scientific Publishing, Singapore, 2018, vol. 1, pp. 241–284.

4 A. Zakutayev, C. M. Caskey, A. N. Fioretti, D. S. Ginley, J. Vidal, V. Stevanovic, E. Tea and S. Lany, *J. Phys. Chem. Lett.*, 2014, **5**, 1117.

5 Y. Zhou, J. Chen, O. M. Bakr and H.-T. Sun, *Chem. Mater.*, 2018, **30**, 6589.

6 J. Euvrard, Y. Yan and D. B. Mitzi, *Nat. Rev. Mater.*, 2021, **6**, 531.

7 E. I. Marchenko, S. A. Fateev, N. N. Eremin, Q. Chen, E. A. Goodilin and A. B. Tarasov, *ACS Mater. Lett.*, 2021, **3**, 1377.

8 V. A. Blatov, *Crystallogr. Rev.*, 2004, **10**, 249.

9 V. A. Blatov, A. P. Shevchenko and D. M. Proserpio, *Cryst. Growth Des.*, 2014, **14**, 3576.

10 L. Pauling, *J. Am. Chem. Soc.*, 1932, **54**, 3570.

11 C. Tantardini and A. R. Oganov, *Nat. Commun.*, 2021, **12**, 2087.

12 T. B. Kinraide, *Environ. Toxicol. Chem.*, 2009, **28**, 525.

13 J.-W. Xiao, Y. Liang, S. Zhang, Y. Zhao, Y. Li and Q. Chen, *Chem. – Eur. J.*, 2019, **25**, 2597.

14 D. J. Kubicki, D. Prochowicz, A. Hofstetter, B. J. Walder and L. Emsley, *ACS Energy Lett.*, 2020, **5**, 2964.

15 W. Xiang, Z. Wang, D. J. Kubicki, X. Wang, W. Tress, J. Luo, J. Zhang, A. Hofstetter, L. Zhang, L. Emsley, M. Grätzel and A. Hagfeldt, *Nat. Commun.*, 2019, **10**, 4686.

16 G. Pan, X. Bai, D. Yang, X. Chen, P. Jing, S. Qu, L. Zhang, D. Zhou, J. Zhu, W. Xu, B. Dong and H. Song, *Nano Lett.*, 2017, **17**, 8005.

17 J.-S. Yao, J. Ge, B.-N. Han, K.-H. Wang, H.-B. Yao, H.-L. Yu, J.-H. Li, B.-S. Zhu, J.-Z. Song, C. Chen, Q. Zhang, H.-B. Zeng, Y. Luo and S.-H. Yu, *J. Am. Chem. Soc.*, 2018, **140**, 3626.

18 F. Wang, R. Deng, J. Wang, Q. Wang, Y. Han, H. Zhu, X. Chen and X. Liu, *Nat. Mater.*, 2011, **10**, 968.

19 B. Zhou, L. Tao, Y. Chai, S. P. Lau, Q. Zhang and Y. H. Tsang, *Angew. Chem., Int. Ed.*, 2016, **55**, 12356.

20 Y. T. An, C. Labbé, J. Cardin, M. Morales and F. Gourbilleau, *Adv. Opt. Mater.*, 2013, **1**, 855.

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