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Theoretical assessment of thermodynamic stability of 2D octane-1,8-diammonium lead halide perovskites

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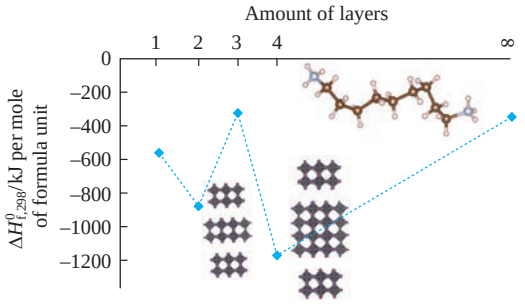
Two-dimensional (2D) lead halide perovskites are promising materials for photovoltaics due to a combination of excellent functional properties and improved stability as compared to their 3D analogues. A thermodynamic stability of the 2D octane-1,8-diammonium-based perovskites containing one to four layers has been assessed using a semi-empirical approach. Revealed values of the standard enthalpy of formation are essentially negative, while the dependence of enthalpy on the number of layers is not linear, so the perovskites with the even number of layers seem to be much more stable due to the features of their crystal and local structures.



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The 2D halide perovskites have recently become considered as highly promising semiconductors possessing a high degree of the structural flexibility, tunable optoelectronic properties, and stability much better than that of 3D hybrid perovskites.[1–7] To technologically develop these materials, it is of great importance to understand their thermodynamic stability, fundamental synthetic limitations, and the derived structure–property relationships. An application of theoretical approaches based on semi-empirical atomistic transferable models of the interatomic interaction potentials[8] and machine learning models for the calculations of local charges[9] allowed us to explore fundamental properties of such a material.[†,10–17]

The structure of 2D perovskites can be constructed *via* 'slicing' of traditional 3D perovskite across different planes, resulting in (100)-, (110)- and (111)-oriented perovskite families. Nowadays the (100)-oriented 2D perovskites are the most common, whose general formula is $(A')_2(A)_{n-1}M_nX_{3n+1}$ or $(A')(A)_{n-1}M_nX_{3n+1}$, where A′ is one- or twofold charged organic cation (respectively) acting as a spacer between the perovskite layers, and A is a onefold charged cation [methylammonium (MA^+), or formamidinium (FA^+), or Cs^+], M is a metal ion (Ge^{2+}, Sn^{2+}, or Pb^{2+}), and X is a halide one (Cl^-, Br^-, or I^-).[18]

The 2D network itself consists of inorganic perovskite layers formed by the corner-sharing MX_6 octahedra. Large cations of the organic spacer are bound to the inorganic layers by electrostatic interactions between the ammonium groups and halide anions. There are two structural parameters that can be tuned in 2D perovskites: the cationic spacer (an aliphatic or aromatic ammonium cation), whose shape and size influence the structural type of perovskite; and the number of perovskite layers (n), which defines the layer thickness and the band gap of material.

Specifically, as n increases, the band gap (E_g) decreases due to the reduced electronic and quantum confinement, reaching the E_g of typical three-dimensional hybrid halide perovskites AMX_3 as a limit at $n \to \infty$.[1]

Herein, we report the calculations of local charges, crystal chemical analysis, and semi-empirical thermodynamic calculations for a broad family of 2D octane-1,8-diammonium-based perovskites, $(NH_3C_8H_{16}NH_3)(MA)_{n-1}Pb_nI_{3n+1}$ (n = 1–4). Figure 1 shows their structures based on the experimental data.[19] The effective charge at the atoms in the structure of 2D halide perovskites is one of the key factors determining the distortion degree for the octahedral layers. To calculate the local charges, we used a novel machine learning algorithm[9] successfully applied for the case of metal-organic frameworks. Here, we show for the first time that the

[†] To determine the degree of distortion of BX_6 octahedra, the following equation introduced by J. A. Alonso[10] was used: $\Delta d = 1/6\Sigma[(d_n–d)/d]$, where d_n are the individual Pb–I distances, and d is the arithmetic mean of those distances.

All the semi-empirical calculations were performed using the GULP 5.0 program.[11] In the total lattice energy value, which is calculated by atomistic computer simulations in addition to the structural energy containing the long-range coulomb contribution and contributions from shorter-range interactions, the charge transfer energy was also taken into account and calculated according to the known algorithm.[12]

The computation-ready, experimental metal-organic frameworks (CoRE MOFs) database[13–15] was used as a reference set for implementing the partial charge model. Atomic point charges for 2932 MOFs[16] obtained with the density-derived electrostatic and chemical (DDEC) charge partitioning method were used for the training and/or validation of presented model.[9] The crystal structures were visualized using the VESTA program.[17]

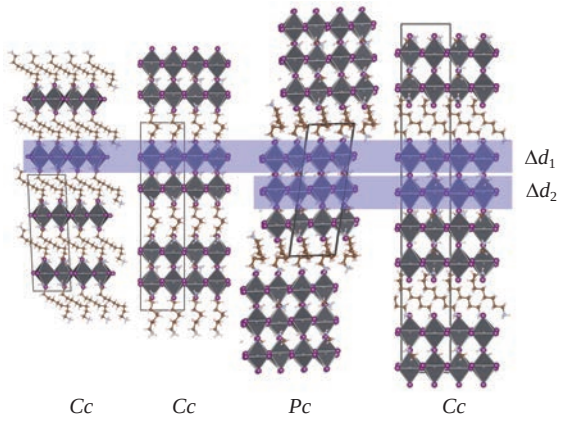

Figure 1 Crystal structures of $(NH_3C_8H_{16}NH_3)(MA)_{n-1}Pb_nI_{3n+1}$ perovskites (n = 1–4), the view from (xz) plane. Distortions of PbI_6 octahedra are shown for different layers as Δd_1 and Δd_2. The estimated Δd_1 values are equal to 3.49×10^{-5}, 2.11×10^{-4}, 6.66×10^{-4}, and 7.33×10^{-4} for compounds containing from 1 to 4 (n) layers, respectively. The Δd_2 values are 1.26×10^{-4} and 3.22×10^{-4} for n = 3 and 4, respectively.

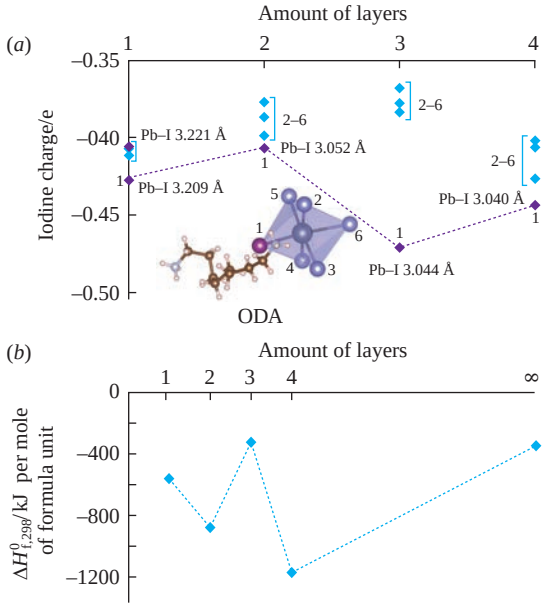

Figure 2 Plotted results of structure and stability estimation: (*a*) charge distributions at iodine atoms in octahedra for 2D lead halide perovskite with ODA cation, where the number 1 shows the terminal iodine atoms, and 2–6 correspond to the other iodine atoms in the PbI_6 octahedra; and (*b*) calculated values of the standard enthalpy of formation for 2D $(NH_3C_8H_{16}NH_3)(MA)_{n-1}Pb_nI_{3n+1}$ (n = 1–4) and 3D $MAPbI_3$ from elements.

charge at the terminal iodine ions in the octahedra decreases upon increasing the number of layers [Figure 2(*a*)]. It is worth to note that the charge at the terminal iodine atoms is lower due to the shorter terminal Pb–I bond in the octahedra as compared to the other bonds. At the same time, the band gap in this series of compounds decreases with the growing number of octahedral layers from 2.43 eV (n = 1) to 1.90 eV (n = 4),[19] which correlates with a decrease in the terminal Pb–I distances in the octahedra.

Considering the estimated distribution of local charges in the structures,[‡] we calculated the standard enthalpy of formation (ΔH_f^0) for experimental 2D compounds $(NH_3C_8H_{16}NH_3)(MA)_{n-1}Pb_nI_{3n+1}$ (n = 1–4)[19] from elements using the model of interatomic potentials that has proven itself in modeling of 3D $MAPbX_3$ (X = I or Br) solid solutions.[8] The ΔH_f^0 values [Figure 2(*b*)] are negative for all the investigated compounds with n = 1–4. However, the dependence of these values is nonlinear, and the compounds possessing an even number of layers (n = 2 or 4) demonstrate that their standard enthalpy of formation is strongly lower (ΔH_f^0 = −880.6 kJ mol^{-1} for n = 4 and –1172.0 kJ mol^{-1} for n = 2). Corresponding enthalpies for the compounds containing an odd number of the layers (n = 1 or 3) are significantly smaller than that for 'even' ones. Thus, the trend for the compounds with an odd number of layers also seems to be opposite, since the standard enthalpy of formation becomes less exothermic upon increasing n (ΔH_f^0 = −563.6 kJ mol^{-1} for n = 1 and –325.7 kJ mol^{-1} for n = 3).

The acquired data allowed us to assume that the planning of preparation routes for new families of layered perovskites should be considered as a complex task, and it would not be expected that the number of layers in those phases is a simple parameter that guarantees a better thermodynamic stability and, thus, the opportunity of wider using the perovskites in solar energy or optoelectronic devices. A proper simulation of the structure and the computer search for suitable band gaps of such perovskites should be performed prior to the selection of a certain synthetic approach. This is a way to reduce efforts to technologically implement new phases. A special point of interest is that the variation in the number of perovskite layers changes drastically their local structure in terms of distortions of the lead–halogen polyhedra. The layers seem to be structurally non-uniform, and the outer polyhedra in the closest proximity of cations would experience larger distortions and deeper charge changes. The latter affects other functional properties of the perovskites, such as conductivity, making them extra sensitive to the number of layers in the structure. Obviously, this does not necessarily correlate with the band gap itself and the phase stability as two primary properties expected to be improved.

In conclusion, the considered unique structural complexity suggests an algorithm allowing one to select the most practically relevant phases among the layered perovskites *via* a pure simulation preceding their experimental preparation and technological processing. First of all, the cation composition and the number of layers in perovskites should be examined in order to suggest a widen set of the relevant phases possessing a required band gap range and a better thermodynamic stability. Then, the set should be optimized through the analysis of distortions of the lead–halogen conductive network. The last but not least step includes a selection of the remaining most relevant phases *via* minimizing the number of layers present under the other equal conditions, since a larger number usually complicates conditions of the experimental preparation. The reported findings evidence for a great practical importance of the theoretical evaluation of new layered perovskites possessing a high structural complexity.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.05.005.

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[‡] See Online Supplementary Materials for the simulated .cif file.

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