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Relative distance from the center of mass – a new structural descriptor linking the structure of organic cations with inorganic framework distortions in layered hybrid halide perovskites

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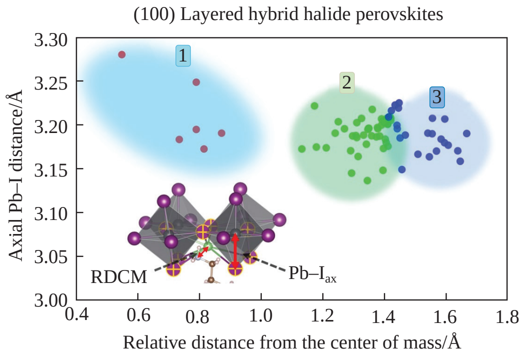
The rational design of layered hybrid lead halide perovskites (LHHPs) for photovoltaics is still difficult due to complex relationships between structural parameters and functional properties. We propose to consider the Relative Distance from the Center of Mass (RDCM) of a void in the inorganic framework to the center of positive charge of the organic cation as a new structural descriptor that makes it possible to clarify the dependence of the geometry of the inorganic framework on the structure of interlayer organic cations, which have a significant effect on the optoelectronic characteristics of LHHPs.



Keywords: hybrid perovskites, layered structures, composition–structure–property relationships, lattice distortions, crystal chemistry.

Layered hybrid halide perovskite-derived materials (LHHPs) have recently emerged as promising semiconductors with a high degree of structural flexibility and tunable optoelectronic properties.[1–7] Understanding composition–structure–property relationships is especially important for the rational design of these materials. One of the key characteristics of LHHPs is the band gap energy, which is almost completely determined by the configuration of the inorganic framework, while the nature and packing of organic cations affect the band gap indirectly through the distortion of inorganic layers.[8,9] However, designing LHHPs with a target band gap value is a nontrivial task due to the complex relationship between the structure of the organic cation and the resulting structural parameters of the inorganic layer.

Previously, six geometrical descriptors were proposed to describe the inorganic framework: in-plane and out-of-plane distortion angles in layers of octahedra (θ_{in}, θ_{out}),[5,9] distances of axial and equatorial Pb−I bonds (d_{ax}, d_{eq}), the layer shift factor and interlayer distances between adjacent layers of octahedra (d_{int}). It is shown that d_{int}, θ_{in} and d_{ax} have the greatest influence on the band gap,[10] of which the descriptor d_{int}, in turn, is mainly determined by the size and packing of interlayer organic cations, while θ_{in} and d_{ax} are related to such structural features of organic cations as the steric effect index, eccentricity, largest ring size and hydrogen bond donor capacity.[11] However, to describe the relationship between organic and inorganic layers in the homologous series of LHHPs with different numbers of layers of PbI_6 octahedra, only one descriptor is proposed, namely the so-called penetration depth[12–14] [Figure 1(*b*)].

The penetration depth was introduced as the distance between two geometric planes: the averaged plane of the axial halogen atoms in the perovskite inorganic layer and the plane parallel to the first one and passing through the positively charged nitrogen atoms of organic cations.[16] It has been shown for some structures that the penetration depth into inorganic slabs correlates with the average tilt angle between PbI_6 octahedra.[13,16] However, this is not a general rule, and plots of axial Pb–I distances and Pb–I–Pb angles for 70 experimentally refined (100) LHHP structures from the 2D perovskite database[16] do not show a clear correlation with penetration depth values (Figure 2). This can be explained by the fact that the penetration depth is a purely geometrical parameter that indirectly reflects the result of the Coulomb interaction of the positively charged $-NH_3^+$ functional group with eight negatively charged iodine atoms of the inorganic layer, which form a half of the

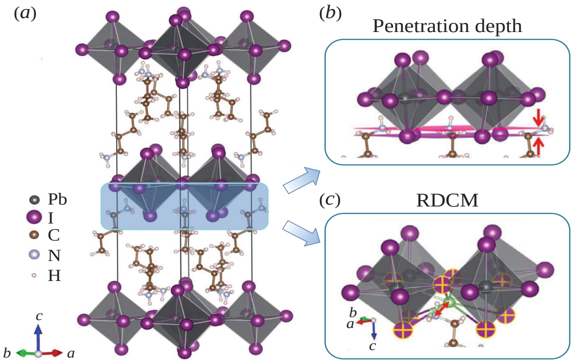


Figure 1 (*a*) Crystal structure of $(BA)_2PbI_4$ (BA = butylammonium)[15] related to (100) LHHPs and graphical definitions of (*b*) penetration depth and (*c*) RDCM. The green ball indicates the position of the center of mass of the selected eight iodide ions.

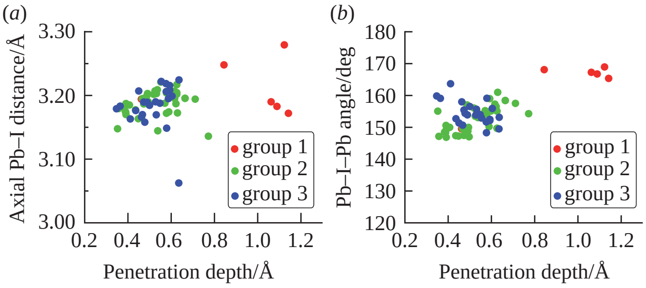


Figure 2 (*a*) Average axial Pb–I distances and (*b*) Pb–I–Pb angles for (100) LHHPs depending on the penetration depth of organic cations into the inorganic layer.

cuboctahedral void, and the formation of hydrogen bonds between the inorganic framework and the interlayer cation. The division of cations into groups is further described in Figure 2.

To take into account the complex nature of the interaction between organic cations and the inorganic framework, we propose a new geometrical descriptor, Relative Distance from the Centre of Mass (RDCM) [Figure 1(*c*)]. RDCM is defined as the distance between the center of positive charge of the organic cation and the center of mass of the inorganic framework void. On the one hand, this distance depends on the Coulomb interaction of positively and negatively charged ions in the structure. On the other hand, RDCM is affected by more complex interactions of organic cations with the inorganic framework or with each other.

As can be seen in Figure 3, the values of the axial Pb–I distances and the Pb–I–Pb angles in (100) single-layered LHHPs on the RDCM dependence plot are distributed more homogeneously than on the penetration depth dependence plot. In addition, a more detailed consideration of the structures allows us to divide them into three groups according to the type of interlayer organic cation: (1) cations with more than one hydrogen-bond-donating charged group that interacts with axial iodide ions (RDCM 0.5–1.0 Å), (2) predominantly unbranched alkylammonium cations without a single hydrogen-bond-donating group that interacts with axial iodide ions (RDCM 1.17–1.41 Å) and (3) cations with hindered hydrogen-bonding due to steric or other reasons (RDCM 1.42–1.65 Å) (see Figure 3).

LHHPs of the first group with low RDCM values consist of organic cations with imidazolium or piperidinium rings, which provide multiple hydrogen bonding centers and, therefore, enhance the interactions of the cation with the negatively charged inorganic layer. Such a strong interaction leads to an elongation of the axial Pb–I bonds, reaching a length of 3.27 Å for this group of cations (see Figure 3). The second group of structures has average RDCM values between groups (1) and (3). In terms of the number of structures, the second group is the most numerous and consists mainly of alkylammonium cations with various chain lengths. Conformational flexibility and different possible packing of these cations in LHHP structures lead to a significant range of the axial Pb–I bond lengths in this group. The RDCM values for the third group of LHHPs are greater than those for the first and second groups. Most of the structures in this group are built by monoalkylammonium cations containing a bulky α- or β-branched carbon chain, resulting in a large steric angle of substituent. The presence of such substituents leads to steric hindrance for effective hydrogen bonding and, consequently, to an increase in the distance between the centers of mass of positive and negative charges. Cations of another type from the third group of LHHPs with similar RDCM values contain functional groups with hydrogen bond acceptors, such as –OH or –COOH, which compete with axial iodine atoms for hydrogen bonds of the cation and thus also significantly weaken the NH···I interaction.

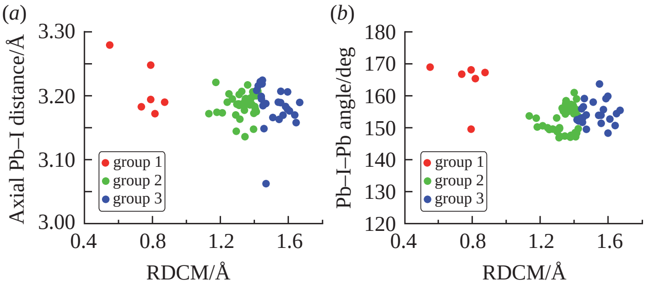


Figure 3 (*a*) Average axial Pb–I distances and (*b*) Pb–I–Pb angles for (100) LHHPs depending on the RDCM value.

To sum up, we present a new geometrical descriptor for layered hybrid halide perovskites, namely the Relative Distance from the Centre of Mass (RDCM) of the inorganic framework void to the center of positive charge of the organic cation. Using the RDCM descriptor, we rationalized the relationship between the structure of organic interlayer cations and distortions of the inorganic framework for a set of (100) LHHP structures. This study is a step towards understanding the relationship between the structure of organic cations and the distortion of inorganic frameworks of LHHPs, allowing rational design of new LHHP materials.

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