Supplementary information for

Exploring the orthorhombic-tetragonal phase transition in $CH_3NH_3PbI_3$: The role of atom kinetics

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1 Unit cell transformations

In this study, both orthorhombic and tetragonal unit cells are defined by considering the minimal cell of the cubic $Pm\overline{3}m$ structure (that contains 12 atoms) and performing the following transformation:

$$\begin{pmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{pmatrix}_{Pnma} = \begin{pmatrix} 1 & -1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \begin{pmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{pmatrix}_{Pm\overline{3}m}$$

We point out that often the **c** axis of the $Pm\overline{3}m$ structure is conventionally mapped to the **b** axis of the $Pnma$ structure [1], whereas mapped to the **c** axis of the tetragonal phase. Here, we consider the same mapping for both orthorhombic and tetragonal structures (see figure 1), in order to highlight the clear relationship between the two unit cells.

2 Models with different MA^+ configurations

Figure 2 shows the structural properties of four atomic models with their MA^+ ions always standing within the **a**-**b** crystallographic plane, but having different orientations. Model (a) represents the standard orthorhombic model [2, 3], with

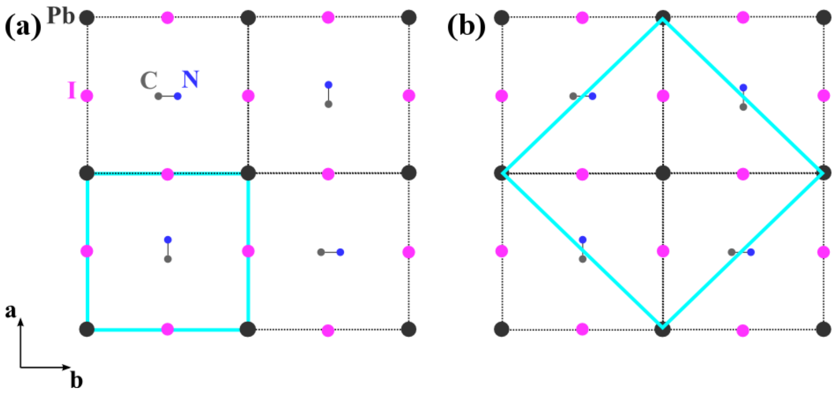

Figure 1: Schematic representation of the transformation between (a) the cubic $Pm\bar{3}m$ unit cell and (b) the orthorhombic $Pnma$ or tetragonal $I4cm$ unit cell, projected on the **a**-**b** crystallographic plane.

the optimized axis parameters from our density functional theory calculations being |**a**|=9.16 Å, |**b**|=8.69 Å and |**c**|=12.99 Å. Model (b) derives from structure (a) by rotating half of the MA$^+$ ions on the **a**-**b** plane in order to obtain a perfectly parallel alignment with respect to the **c** crystallographic direction. Its total energy is higher than model (a) by 221 meV. Model (b) preserves the orthorhombic character of the axis parameters with |**a**|=9.22 Å, |**b**|=8.64 Å and |**c**|=12.97 Å. However, as the MA$^+$ ions are ideally parallel with respect to the **c** direction, this structure has a lower symmetry when compared to model (a). In this sense, it's unit cell can be represented by a $(\sqrt{2}\times\sqrt{2}\times 1)$ supercell of the cubic $Pm\bar{3}m$ space group, rather than the $(\sqrt{2}\times\sqrt{2}\times 2)$ supercell of model (a). Model (c) is obtained from model (b) by rotating the MA$^+$ ions of the first **a**-**b** plane around their C-N axis by 60°. Such transformation restores the $(\sqrt{2}\times\sqrt{2}\times 2)$ symmetry and lowers the total energy of the system, which now stands higher than model (a) by only 139 meV. This MA$^+$ configuration also equilibrates the **a** and **b** lattice vectors (|**a**|=8.96 Å, |**b**|=9.00 Å and |**c**|=12.98 Å), giving rise to a lattice with tetragonal characteristics. We notice that this structure is spontaneously obtained from our *ab initio* molecular dynamics calculations at room temperature, even when starting from different initial configurations [4]. Finally, in model (d) the MA$^+$ ions point towards four faces of the inorganic framework, without being antialigned with respect to the **c** direction. Such configuration is the most unfavorable with respect to the previous ones, standing energetically higher by 353 meV when compared to model (a). The

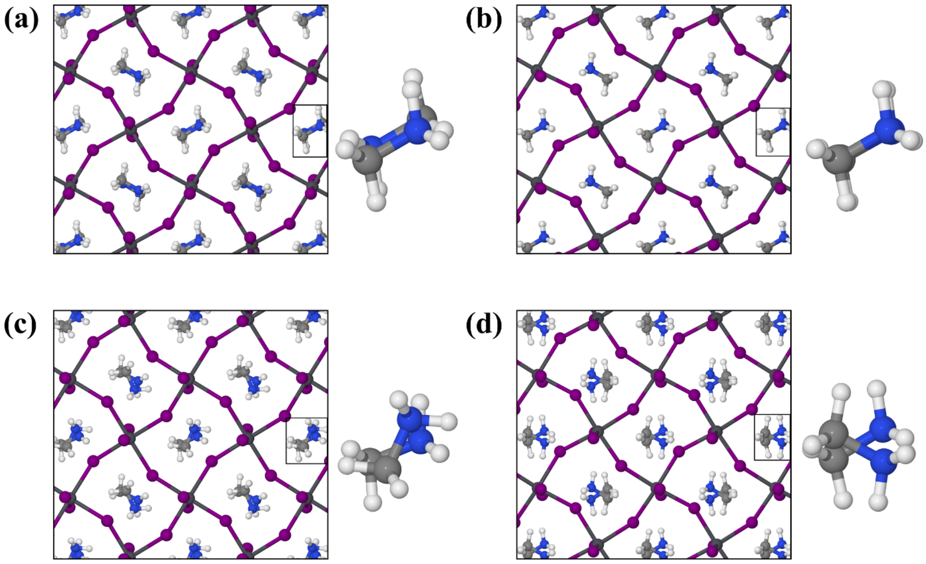

Figure 2: Different models of $CH_3NH_3PbI_3$ with the MA^+ ions standing on the **a**-**b** crystallographic plane but with different relative orientations.

lattice vectors are anisotropic (|**a**|=9.21 Å, |**b**|=8.76 Å and |**c**|=13.04 Å). Models (a) and (c) have been considered as the base models of this study for the orthorhombic and the tetragonal phase, respectively.

References

[1] IP Swainson, RP Hammond, C Soulliere, O Knop, and W Massa. Phase transitions in the perovskite methylammonium lead bromide, ch 3 nd 3 pbbr 3. *J. Solid State Chem.*, 176(1):97–104, 2003.

[2] Yukihiko Kawamura, Hiroyuki Mashiyama, and Katsuhiko Hasebe. Structural study on cubic–tetragonal transition of ch3nh3pbi3. *J. Phys. Soc. Jpn.*, 71(7):1694–1697, 2002.

[3] Tom Baikie, Yanan Fang, Jeannette M Kadro, Martin Schreyer, Fengxia Wei, Subodh G Mhaisalkar, Michael Graetzel, and Tim J White. Synthesis and crystal chemistry of the hybrid perovskite (ch 3 nh 3) pbi 3 for solid-state sensitised solar cell applications. *J. Mater. Chem. A*, 1(18):5628–5641, 2013.

[4] Ioannis Deretzis, Bruno N Di Mauro, Alessandra Alberti, Giovanna Pellegrino, Emanuele Smecca, and Antonino La Magna. Spontaneous bidirectional ordering of ch3nh3+ in lead iodide perovskites at room temperature: The origins of the tetragonal phase. *Sci. Rep.*, 6:24443, 2016.