

## Effects of soft mechanochemical synthesis in MAPbCl<sub>3</sub> powders

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Research interest has increasingly focused on hybrid perovskites MAPbX<sub>3</sub> like [CH<sub>3</sub>NH<sub>3</sub>]<sup>+</sup> (MA), X = I or Cl as future photovoltaic material. It was observed that various entropy contributions (stochastic structural fluctuations, anharmonicity, and softness of the lattice) directly affect the optoelectronic properties of halide perovskite materials. [1][2] At the same time, recent studies show that a synthesis of hybrid perovskites by a purely mechanochemical route is possible and that materials with even better optoelectronic properties can be produced this way. [3][4] In our recent investigation on MAPbCl<sub>3</sub>, we found that phase separation occurs in the orthorhombic low-temperature phase, depending on the grinding intensity. [2] For lightly ground batches, besides the orthorhombic phase “o1” (space group *Pnma*,  $a \approx 11.2$  Å,  $b \approx 11.3$  Å,  $c \approx 11.3$  Å) another orthorhombic phase “o2”, which has the same space group *Pnma* as “o1”, but a smaller crystal lattice ( $a \approx 8.0$  Å,  $b \approx 11.3$  Å,  $c \approx 7.9$  Å) was observed by us. Interestingly, the crystal structure of “o2” corresponds to that of the low-temperature orthorhombic structure of MAPbI<sub>3</sub>. We observed that, when the MAPbCl<sub>3</sub> powder is ground even finer, as it is necessary for EXAFS investigations (for EXAFS a grain size of 1 μm is desired), the proportion of “o2” increases and finally mainly “o2” is present. [2] However, we observed from our Rietveld analysis that different MAPbCl<sub>3</sub> batches with different grinding degrees show the same cubic crystal structure at 180 K as at room temperature. Notably, this seems to be only half the truth for the cubic structure of MAPbCl<sub>3</sub>, since in pair distribution function (PDF) studies on MAPbCl<sub>3</sub> powders, it could be shown that local structural distortion is also present in the room temperature phase. [5] We therefore assume that the local order in the room temperature phase of MAPbCl<sub>3</sub> also differs as a function of grinding.

[1] Katan, C. et al, Nature Materials, 2018, 17, 377

[2] G. Schuck, et. al., <https://arxiv.org/abs/2112.00502>

[3] Leupold, N et. al., Appl. Mater. Interfaces, 2019, 11, 30259

[4] Gil-González E. et al., J. Phys. Chem. Lett. 2021, 12, 5540

[5] Bernasconi, A. et al, J. Phys. Chem. C, 2018, 122, 28265