

Can planar defects explain the ordering phenomena in the low-temperature phase of MAPbCl₃?

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Research interest has increasingly focused on hybrid perovskites MAPbX₃ like [CH₃NH₃]⁺ (MA), X = I or Cl as future photovoltaic material. In our recent investigation on wet-chemically produced MAPbCl₃ powders [1] we could show by Rietveld analysis of temperature-dependent synchrotron XRD data that two orthorhombic structures ("o1" and "o2") can be observed at low temperatures. At the lowest measured temperatures (below 140 K), "o1" and "o2" occur simultaneously, whereby the ratio of "o1" and "o2" depends on the Temperature (Fig. 1) and the degree of grinding with which the powder was prepared [1]. It has been observed that the more intensely the powder was ground (i.e. the more the sample was exposed to mechanical stress), the more phase "o2" is present. Furthermore, it was observed that the cubic room-temperature structure of MAPbCl₃ transforms directly into the two orthorhombic low-temperature structures without an intermediate tetragonal structure. Although the space group of the two MAPbCl₃ crystal structures, "o1" and "o2" is *Pnma*, as in the low-temperature phase of MAPbI₃, the cell of the "o1" crystal structure of MAPbCl₃ is with $a = 2ap$; $b = 2ap$; $c = 2ap$ larger than the analogous cell of the orthorhombic low-temperature structure of MAPbI₃ with $a = \sqrt{2}ap$; $b = 2ap$; $c = \sqrt{2}ap$ (where ap is the primitive cubic perovskite lattice parameter). Whereas in the "o2" structure of MAPbCl₃ the smaller cell ($a = \sqrt{2}ap$; $b = 2ap$; $c = \sqrt{2}ap$) could be observed. The results described in [1] partially correspond to the investigations by Alvarez-Galván et al. however, even three orthorhombic phases were observed by these authors at low temperatures [2]. However, more recent studies by Hu et al. show a completely different temperature dependent ratio of "o1" and "o2" [3].

Preliminary analysis from temperature-dependent synchrotron XRD measurements on mechanochemically prepared MAPbCl₃ (mcMAPbCl₃) powders indicate the absence of the low-temperature orthorhombic phase "o1" observed in wet-chemically prepared MAPbCl₃. However, at the lowest temperatures measured in mcMAPbCl₃, more complex ordering phenomena occur. An overview of the effects observed in the synchrotron powder data in the orthorhombic phase of wet-chemically prepared MAPbCl₃ and mcMAPbCl₃ is given. There is emerging evidence that planar faults play a significant role in the explanation of ordering phenomena monitored in hybrid perovskites. This presentation will provide an overview of the phenomena observed in synchrotron data and of the methods that can be employed to simulate the observed diffraction phenomena.

[1] G. Schuck, et. al., J. Phys. Chem. C, 2022, 126, 5388

[2] C. Alvarez-Galván et al., Cryst. Growth Des. 2019, 19, 2, 918–924

[3] J.-K. Hu et al., Small 2024, 240877