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Investigating All-Inorganic Halide Perovskite Phase Transformations via in-situ 4D STEM Heating Experiments

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Background incl. aims

Halide perovskite materials, in particular Cesium lead-based halides (CsPbX3, where X = Br or Cl), are known in the halide perovskite family due to their promising optoelectronic properties. Understanding any phase transitions in CsPbX3 that would occur under typical device operating conditions is crucial for assessing device thermal stability and structural integrity [1, 2]. This work focuses on elucidating phase transitions in CsPbX3 that occur as a result of thermal variations by utilizing in-situ four-dimensional scanning transmission electron microscopy (4D STEM). This approach captures their structural evolution across a temperature range from sub-ambient to the melting point.

Methods

Energy-filtered 4D STEM data were acquired using a JEOL ARM300F microscope outfitted with a GIF Continuum® and post-GIF K3® detector from Gatan. DigitalMicrograph® version 3.6 and eaSI™ technology were used for in-situ 4D STEM data acquisition. Digital Temperature modulation of the samples was achieved using a DENSsolutions heating holder controlled within DigitalMicrograph and a Gatan LN2 holder for cooling.

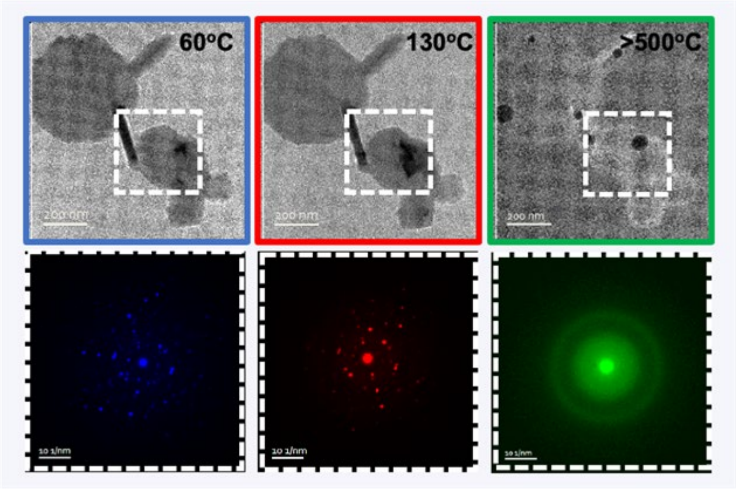
Results

The phase diagram of CsPbBr3 predicts multiple phase transformations as the material is heated from room temperature until its melting point at 500°C. The material begins in an orthorhombic (Pnma) phase and begins a phase transformation to a tetragonal (Cmcm) phase at 88°C, followed by a 2nd transformation to a cubic (P4/mbm) phase at 130°C that persists until the melting point. CsPbBr3 was heated from room temperature until its melting point and initial in-situ 4D STEM data shows temperature-dependent variation in the averaged diffraction patterns, seen in Figure 1. Furthermore, virtual bright field images derived from the in-situ 4D STEM data show dynamic reaction interfaces and evolving contrast during heating. These results emphasize the presence of structural evolution of CsPbBr3 about 60°C, 130°C, and above 500°C.

Conclusion

In-situ 4D STEM data acquisition of CsPbX3 during heating is a powerful methodology for quantitative analysis of the phase evolution of halide perovskites from ambient temperature until their melting point. The data collection tools available with in DigitalMicrograph link 4D STEM data with the experimental temperature profile from the heating holder, providing a detailed chronology of the phase evolution. This allows for a more concrete understanding of the stability ranges of the observed intermediate phases during heating and deeper insight into the material behavior under simulated operational temperatures. Adding complementary techniques such as in-situ electron energy loss spectroscopy (EELS) should provide important chemical information to further assess the structural behavior of CsPbX3 and its consequences on optoelectronic properties.

Graphic:



Keywords:

Halide perovskites, in-situ, 4D STEM

Reference:

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