

## Symmetry Group Determination and Direct Imaging of All-Inorganic Halide Perovskites CsPbBr<sub>3-x</sub>Cl<sub>x</sub>.

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The unique properties observed in halide perovskites originate in their rich structural complexity that allows compatibility with a variety of structural motifs and compounds. Adjustments of the corner-connected BX<sub>6</sub> octahedral network in the ABX<sub>3</sub> structure promote a wide range of optical and electronic properties [1]. For this reason, methods to precisely identify the local symmetry are necessary to unambiguously distinguish different possible structural phases. Here, we determine the crystallography of all-inorganic CsPbBr<sub>1-x</sub>Cl<sub>x</sub> perovskite single crystals, grown *via* the Bridgman-Stockbarger method, by exploring information contained in electron diffraction patterns. Due to the material's sensitivity to the electron beam, precise atomistic studies of halide perovskites by transmission electron microscopy (TEM), scanning TEM (STEM) and electron diffraction are relatively underdeveloped. Consequently, X-ray diffraction has been the technique of choice to assign crystal structures, requiring a careful study of the splitting of certain lines and of the presence of superlattice reflections. Effects due to small atomic shifts can easily be missed in X-ray diffraction, which accounts for reports of incorrect structures. In this work, we use convergent-beam electron diffraction (CBED) acquired at low-temperature (~70K) to identify the symmetry of CsPbBr<sub>3-x</sub>Cl<sub>x</sub> single crystals with x = 0, 1 and 3. High-symmetry CBED pattern containing information on high-order Laue zones (HOLZ), in which the intensities of certain reflections are quite sensitive to small rotations of the octahedral unit, reveal the whole crystal symmetry and positions of Br/Cl anions. Local imaging of the projected atomistic distribution in these crystals is achieved by simultaneous atomic-resolution electron ptychography (a dose efficient diffractive imaging technique [2]) and Z-contrast, using high-speed direct electron detector. A phase transformation dependency on the halide anion is observed as function of composition x. A tetragonal *I4/mcm* structure is assigned to CsPbBr<sub>3</sub> whereas CsPbCl<sub>3</sub> is found to be orthorhombic. [3]

[1] M. R. Filip *et al*, Nat. Commun. **5**, 5757 (2014).

[2] H. Yang, *et al*, Nat. Commun. **7**, 12532 (2016).

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