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The Electron Microscopy of Heterostructures Made of Perovskite Phases in Light Emitting Crystals.

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Three dimensional (3D) perovskites are sensitive materials that often give rise to two dimensional (2D) Ruddlesden-Poper (RP) hybrid perovskites. These 2D materials contain organic spacers that lead to a higher material stability. There has been a recent publication showing the spontaneous formation of 2D/3d heterostructures on the edges of 2D-RP hybrid perovkites that additionally show low energy edge photoluminiscent crystals. Here details on the phase distribution are given with atomic resolution and under low dose conditions. Samples have been synthesized by a method that is described in an earlier publication [1]. The PL images and peak positions of $(BA)_2(MA)_{n-1}Pb_nBr_{3n+1}$ (n = 1, 2, 3) confirm the edge emission for n = 2 and 3 only, in agreement with a previous report [1]. Scanning electron microscopy (SEM) images also confirm that emissive edges $(BA)_2(MA)_2Pb_3Br_{10}$ are smooth, as opposed to the rough edge in $CsPb_2Br_5$ platelets, suggesting that the edge emission does not come from the overgrown or contaminated nanostructures during the synthesis. To determine whether the edge emission is an intrinsic or extrinsic property of the RP perovskites, fresh edges are cut from a large piece of $(BA)_2(MA)_2Pb_3Br_{10}$ by using the tip of a probe and monitored its edge emission. These samples are then prepared for electron microscopy.

The TEAM 0.5 electron microscope from NCEM-Molecular Foundry at the LBNL [2] is used at 80 KeV and in low dose conditions i.e., the samples are observed with a dose of 10 $e^-/Å^2$ s. Image focal series are used with 50 images at different focus setting in order to apply a procedure of exit wave reconstruction. This produces amplitude and phase images with atomic resolution in addition to a spatial resolution of 0.8 Å. In all cases the software MacTempass X is used to determine the reconstructed exit wave, correct for residual aberrations and produce phase and amplitude images. Simulations are performed with the software CrystalKitX.

The electron microscope work is summarized in Figure 1. Experimental images in a focal series are shown as example of the imaging procedure. Although the contrast is not sufficient to judge the phase and atomic distribution, these images at different defocus settings can be used to produce phase and amplitude images with atomic resolution. These particular perovskite samples are rather sensitive to the electron beam, but the image contrast variation in the images of the focal series is related to the different focusing condition. Thus little to none beam damage is found for the electron dose in use. Exit wave reconstruction gives similar results for 25 or for 50 images and there is confidence that the exit wave reconstruction procedure allows to determine the genuine atomic and phase distribution both at the edge and near the center of the crystals, see Fig. 1d. Figure 2 shows an example of the observed phases. Here a phase image of the edge region of a platelet is shown. The electron microscope work shows a phase

distribution with two main components in the exfoliated sample. The edge of the sample is dominated by the $MAPbBr_3$ perovskite while the interior is $BA_2MA_2Pb_3Br_{10}$. The former is obtained by loosing BA. Low dose electron microscopy in transmission mode has been performed to preserve the genuine phase structure, especially in the presence of water, N, C and O. The sample is particularly unstable but still 50 images can be taken at rather low dose (10 e-/Å^{2}s) and 80 keV in the TEAM05 electron microscope of the NCEM-MF [2].

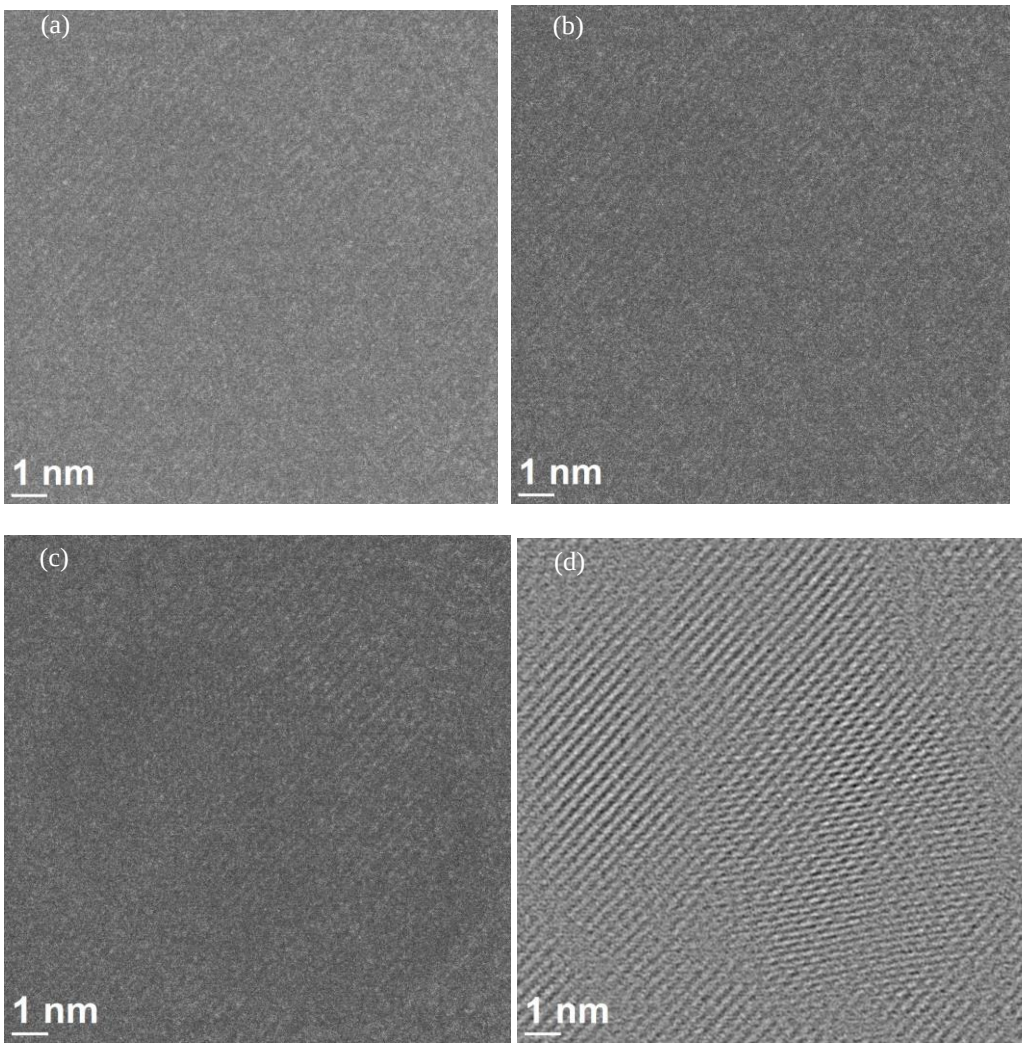

Figure 1. (a-c) Experimental images in a focal series after 1 (a), 10 (b) and 50 (c) focus steps. (d) Phase image showing two different nanograins in the center of the perovskite crystal. The rather low dose allows to keep these beam sensitive phases without any change as compared to the as-synthesized condition.

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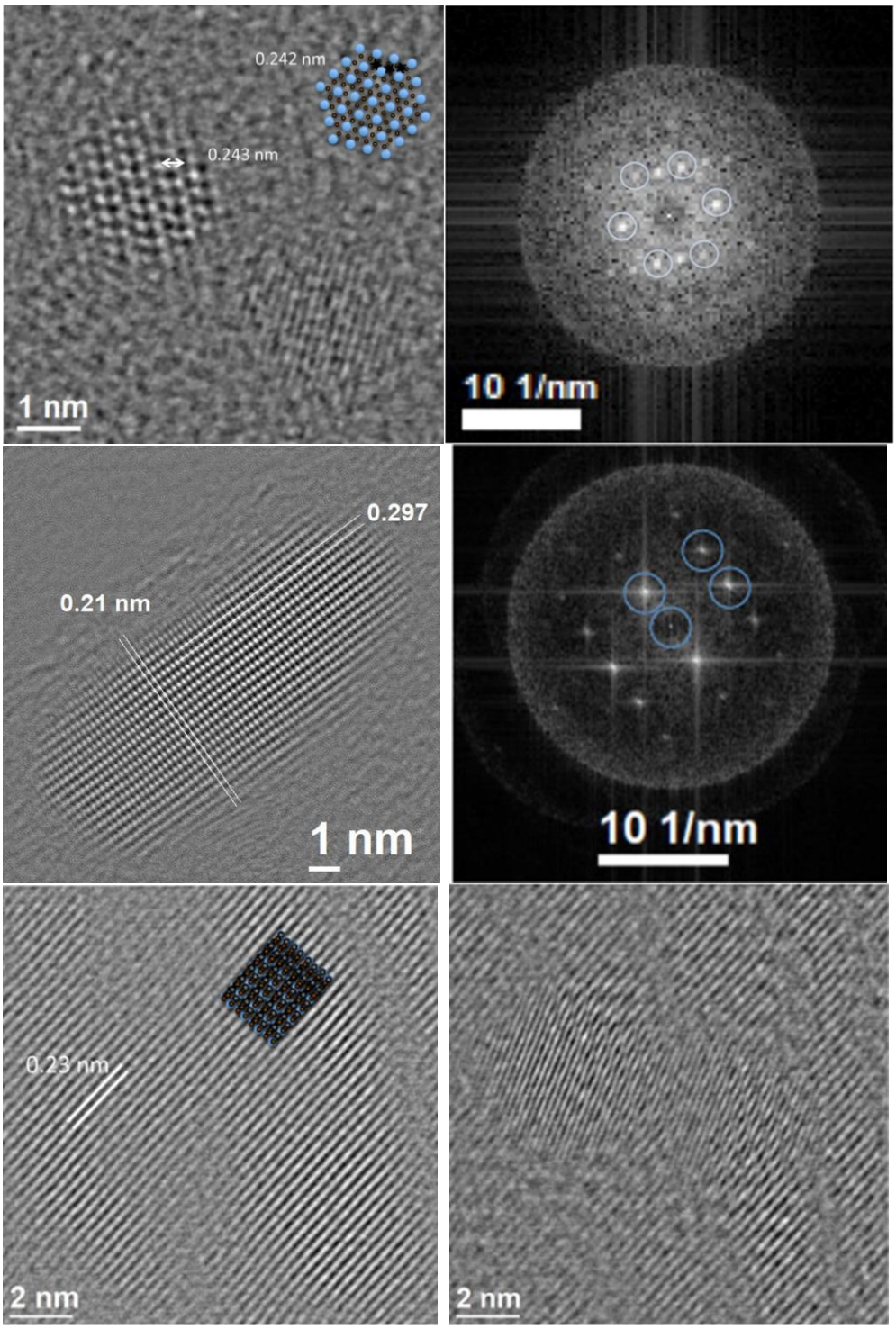

Figure 2. Structural phases in the perovskite crystals as a function of position. (a) Nanoparticle at the edge of crystal with structural simulation for a $MAPbBr_3$ perovskite. (b) Fourier transform with a [111]

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zone axis of (a). (c) Nanoparticle at the edge of the crystal with atomic resolution and (d) corresponding FFT in the [001] zone axis of a $MAPbBr_3$ phase. (e) and (f) Images of $(BA)_2(MA)_2Pb_3Br_{10}$ phase at the center of the crystal. A simulation is superimposed in figure (e). The interior of the crystal has different structural phases as compared to the edge of the crystal where the BA components are lost.

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