

## Elucidating the mechanisms of phase transitions in semiconducting nanostructures via low-exposure, dynamical, *in situ* cathodoluminescence

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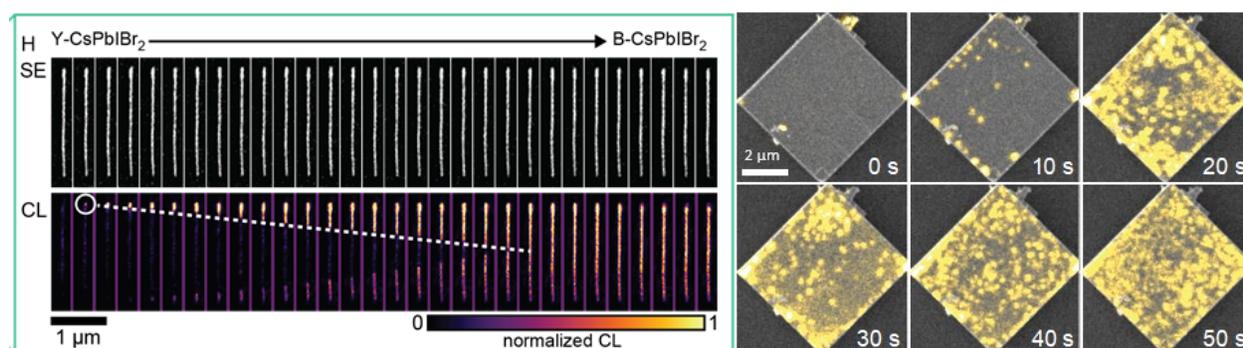
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The microscopic pathways of structural phase transitions are difficult to probe because they occur over multiple, disparate time and length scales. Using *in situ* nanoscale cathodoluminescence (CL) microscopy, we interrogate the thermally-driven transition to the perovskite phase (B-CsPbIBr<sub>2</sub>) in hundreds of non-perovskite phase (Y-CsPbIBr<sub>2</sub>) nanowires and resolve the initial nanoscale nucleation and the subsequent mesoscale growth. We quantify the activation energy for phase propagation and show with molecular dynamics computer simulations that the transformation proceeds via ion diffusion through a disordered interface between the two structures. With the aid of simulation and theory, we show that the original anisotropic crystal structure translates to faster nucleation of the B-CsPbIBr<sub>2</sub> phase at nanowire ends and faster growth along the long nanowire axis. These results represent a significant step towards manipulating structural phases at the nanoscale for designer materials properties.

Time permitting, I will also describe how we elucidate the mechanism for a nanoscale photoinduced compositional phase transition in mixed halide perovskite structures. Photoinduced phase separation in mixed halide perovskites emerges from their electro-mechanical properties and high ionic conductivities, resulting in photoinduced I<sup>-</sup>-rich charge carrier traps that diminish photovoltaic performance. Whether photoinduced phase separation stems from the polycrystalline microstructure or is an intrinsic material property has been an open question. We investigate the nanoscale photoinduced behavior of single-crystal mixed Br<sup>-</sup>/I<sup>-</sup>-methylammonium (MA<sup>+</sup>) lead halide perovskite (MAPb(Br<sub>x</sub>I<sub>1-x</sub>)<sub>3</sub>) nanoplates, eliminating effects from extended structural defects. Even in these nanoplates, we find that phase separation occurs, resulting in I<sup>-</sup>-rich clusters that are nucleated stochastically and stabilized by polarons. Upon lowering the electron-phonon coupling strength by partially exchanging MA<sup>+</sup> for Cs<sup>+</sup>, a phase-separated steady state is not reached, nevertheless transient I<sup>-</sup> clustering still occurs. Our results, supported by multiscale modeling, demonstrate that photoinduced phase separation is an intrinsic property of mixed halide perovskites, the extent and dynamics of which depends on the electron-phonon coupling strength.

## References:

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- [4] We thank E. Wong, E. S. Barnard, D. F. Ogletree, and S. Aloni at the Molecular Foundry for assistance with CL equipment and helpful discussions. CL and analysis work by C.G.B. and N.S.G. has been supported by STROBE, A National Science Foundation Science & Technology Center under Grant No. DMR 1548924. The CL imaging at the Lawrence Berkeley Lab Molecular Foundry and the TEM imaging at the National Center for Electron Microscopy were performed as part of the Molecular Foundry user program, supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. N.S.G. also acknowledges an Alfred P. Sloan Research Fellowship, a David and Lucile Packard Foundation Fellowship for Science and Engineering, and a Camille and Henry Dreyfus Teacher-Scholar Award. Modeling by D.T.L., materials fabrication and characterization by P.Y. and co-workers is supported under the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division under Contract No. DE-AC02-05-CH11231 within the Physical Chemistry of Inorganic Nanostructures Program (KC3103). Molecular dynamics simulations have also been partially supported by the National Science Foundation under NSF-REU grant CHE-1659579. The support and resources of the Center for High Performance Computing at the University of Utah are gratefully acknowledged.



**Figure 1.** Left: Secondary electron and cathodoluminescence movie frames to track structural conversion at 163 °C. Adjacent snapshots are separated in time by 6 seconds. Right: photoinduced phase separation of iodide and bromide revealed in nanoplates.