

Effect of adding a large A cation to self-healing rates of $\text{CH}_3\text{NH}_3\text{PbI}_3$

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Self-healing (SH) of halide perovskites (HaPs) is likely one of the most important of the many important HaP properties. It can play a direct role in many other properties, such as defect density, charge lifetimes and, of course, device stability. Here we show that in *polycrystalline film* form, which is how they are used most commonly in devices, >10 at.% substitution of methylammonium, MA^+ , on the A site of APbI_3 , with the large cations, guanidinium (Gua^+) or acetamidinium (AA^+), significantly increases the compounds' recovery kinetics from damage. Substitution with dimethyl ammonium (DMA^+), which is about the same size as Gua^+ or AA^+ , does not affect the SH rate. Based on the time scale of the SH, we infer that the rate-determining step of the SH involves short-range diffusion of A^+ and/or Pb^{2+} cations. Correlations have been found between the SH rate and strain (from the large cations), dipole moment of the A^+ cation and A^+-I^- hydrogen bonding, which may offer clues for a more detailed mechanism of SH and understanding of SH kinetics. Fast recovery kinetics are important from the device perspective as they will allow complete recovery in *operando* devices, or when switched off (LEDs) / in the dark (PV).