

Toward kinetic stabilization of halide migration in pure and mixed-halide perovskite

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INTRODUCTION

The easy bandgap tunability of mixed-halide perovskites by changing the ratio of halides in the chemical composition makes them promising candidates for LEDs and tandem solar cells. However, illuminating the material results in formation of phases rich in one of the halides (phase-segregation). Similarly, pure halide compositions have been shown to suffer from ion migration reducing the long-term stability of the solar cell. Activation energies reported for the two processes are comparable^{1,2}, suggesting vacancy-mediated anion transport in both cases.

We investigate the kinetics of phase segregation in mixed halide perovskite MAPb(Br_xI_{1-x})₃ (x_{Br} = 0.5) by transient absorption spectroscopy under hydrostatic pressure using an additional light beam to induce phase segregation during the measurement (**Figure 1**). We observe a slower build-up of the bromide and iodide-rich phase (**Figure 2**) when the pressure increases from ambient pressure to 0.3 GPa.

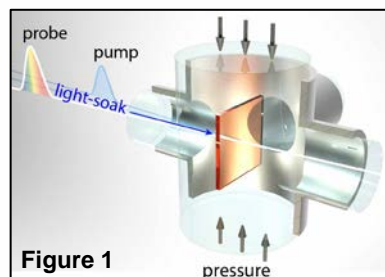


Figure 1

The **degradation rate** resulting from halide migration is proportional to the diffusion coefficient of mobile ions D

$$\tau_{deg} \propto D = l_D^2 \omega_0$$

$$\tau_{deg} = \frac{\epsilon_0 \epsilon k_B T}{q^2 N D_0} e^{\frac{E_A}{k_B T}}$$

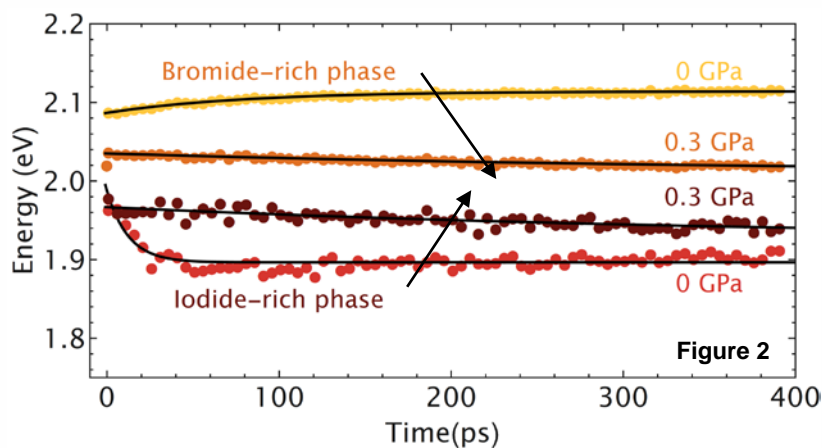


Figure 2

RESULTS AND DISCUSSION

A common explanation for halide migration is the presence of trap states inducing halide accumulation via the electric field from the trapped holes. Theoretical calculations (shown in **Figure 3a**) show the increase of activation energy as function of pressure (this alone would induce decrease in segregation rate). This trend seems to be followed also by experimental results in **Figure 3b** where the $\ln(\tau_{iodide})$ scales with the activation energy and increases as function of pressure.

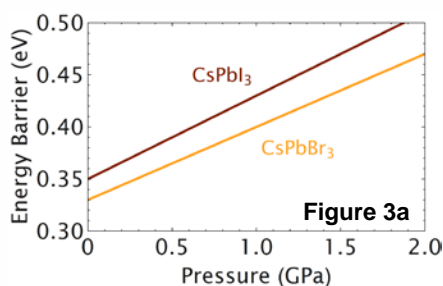


Figure 3a

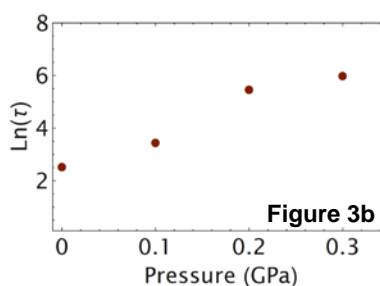


Figure 3b

CONCLUSION

In this work we conclude that halide migration in mixed-halide system is slower under pressure and almost fully suppressed at 0.3 GPa. We interpret this as a change in the activation energy as $\ln(\tau)$ follows the same trend as the theoretical activation energy calculated under pressure. This would suggest that a similar approach can be used to suppress halide migration in pure system.