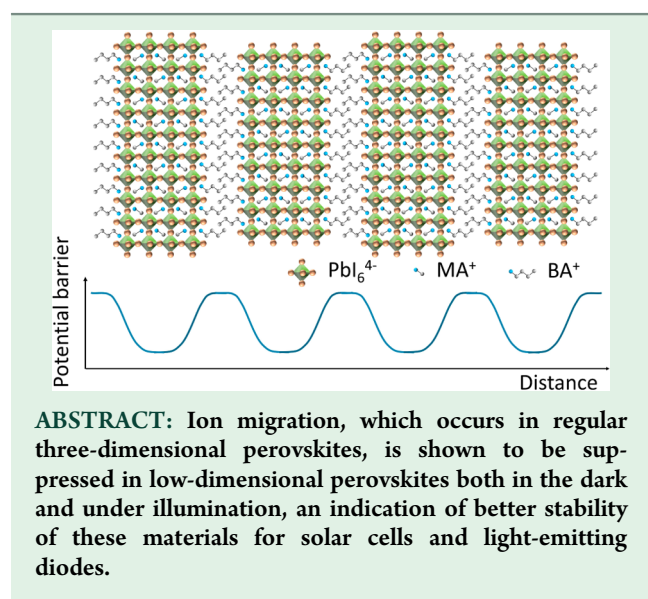


Suppressed Ion Migration in Low-Dimensional Perovskites

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ABSTRACT: Ion migration, which occurs in regular three-dimensional perovskites, is shown to be suppressed in low-dimensional perovskites both in the dark and under illumination, an indication of better stability of these materials for solar cells and light-emitting diodes.

Organic–inorganic hybrid perovskites are gaining increasing attention in the optoelectronic fields for their applications in solar cells, light-emitting diodes, photodetectors, and radiation detectors.¹ However, the intrinsic stability of regular three-dimensional (3D) perovskites such as $\text{CH}_3\text{NH}_3\text{PbI}_3$ is limited by the very small formation enthalpy of -0.05 eV,² which hinders their applications in the real world. Low-dimensional perovskite materials have been shown to possess much larger formation energy and exhibit enhanced ambient stability.^{3,4} The efficiencies of two-dimensional (2D) perovskite solar cells were lower than 5% at the earlier stage of research because of the low mobility of charges for transporting between the sheets crossing the thicker organic spacing ligand.^{3,4} Recently, a breakthrough has been made by aligning the crystallographic planes of the inorganic perovskite component to be vertical to the substrates using a hot-casting method, which increased the efficiency of the layered perovskite solar cells to 12.5%.⁵ A higher efficiency of 15.3% by increasing the layer (n) values in low-dimensional perovskites has been reported.² One issue arising with the quantum confinement effect of the low-dimensional perovskites is that the exciton binding energy is far beyond the thermal activation energy at room temperature. It was proposed that the layer-edge-states (LES) with lower band gap contribute to the dissociation of excitons into free-carriers in Ruddlesden–Popper perovskites with $n > 2$.⁶

Recent studies show the improved ambient stability and thermal stability of the low-dimensional perovskite films, while there is no study yet on the ion migration stability in these materials, which represents a big concern for the 3D perovskites for solar cell applications.⁷ The low-dimensional perovskites have been employed in field-effect transistors⁸ and in light-emitting devices.^{9,10} These devices generally operate under large applied electric field and thus need an even much lower ion migration rate for a reasonable stability.

In this Energy Express, we investigate the ion migration stability in the Ruddlesden–Popper type low-dimensional perovskites by measuring the ion conductivity and ion migration activation energy. The crystal structure of 2D perovskites $(\text{BA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$ ($n = 4$) used in this study is shown in the Abstract graphic; these perovskites have been reported to yield the highest efficiency among 2D perovskites with the layer (n) values less than six. The anionic inorganic layers are separated from one another by the organic n -butylammonium (BA) spacer cations. These layered structures stack together to form 2D perovskites. The X-ray diffraction (XRD) pattern is shown in Figure 1a. Three diffraction peaks at 14.20° , 28.48° , and 43.28° are indexed to be $(\bar{1}\bar{1}\bar{1})$, (202) , and (313) crystallographic planes, respectively.⁵ The optical absorption and photoluminescence spectra of perovskite films are shown in Figure 1b. The PL peak position gives an optical band gap of 1.70 eV. No obvious excitonic absorption peak was observed, indicating that the excitons are almost ionized into free carriers at room temperature by the presence of the LES in $(\text{BA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$.⁶ The top-view and cross-sectional scanning electron microscopy (SEM) images are shown in Figure 1c. The pinhole-free films formed by regular hot-casting method without antisolvent.

The activation energy of ionic conductivity can quantitatively characterize the rate of ion migration, which can be extracted from the temperature-dependent electrical conductivity by the Nernst–Einstein relation: $\sigma(T) = (\sigma_0/T) \exp(-E_a/KT)$, where k is the Boltzmann constant, σ_0 a constant, and T temperature. The device geometry for conductivity measurement is shown in Figure 1d. The temperature-dependent conductivity was measured in the dark and under 0.25 sun illumination for both 3D $\text{CH}_3\text{NH}_3\text{PbI}_3$ and 2D $(\text{BA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$ films (Figure 1e,f). The conductivity in the low-temperature region is mainly ascribed to electronic conduction, because ion migration is suppressed. For the 3D $\text{CH}_3\text{NH}_3\text{PbI}_3$ film, when temperature is

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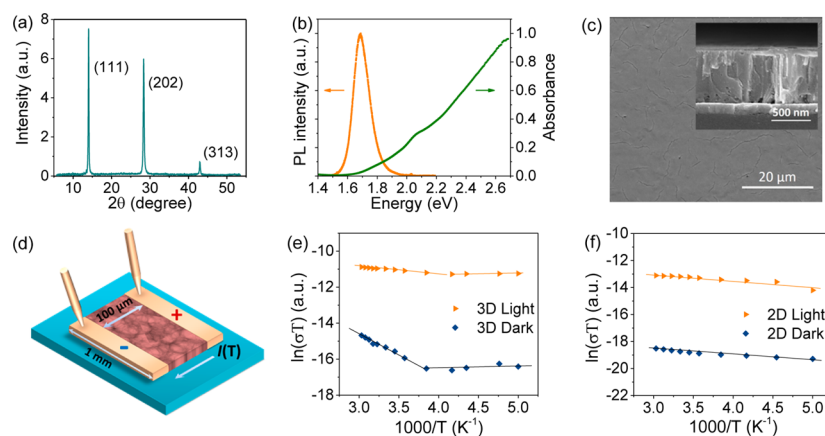


Figure 1. XRD (a), absorption and photoluminescence spectrum (b), and SEM image (c) of 2D perovskite $(\text{BA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$ films; temperature-dependent conductivity measurement geometry (d) and the results of MAPbI_3 (e) and $(\text{BA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$ (f) polycrystalline films.

increased to 260 K, ionic conductivity begins to dominate the total conductivity. The activation energy for ion conduction was fitted to be 0.19 eV in the dark and reduced to 0.03 eV under 0.25 sun illumination. The large activation of 0.19 eV is assigned to ion migration, and small activation of 0.03 eV agrees well with previous reports.¹¹ The transition temperature for electronic- to ion migration-dominated conduction was also reduced from 260 K in the dark to 240 K under illumination. It should be noted that the activation energy of ion migration in 3D $\text{CH}_3\text{NH}_3\text{PbI}_3$ is sensitive to the grain size and crystallinity of the 3D $\text{CH}_3\text{NH}_3\text{PbI}_3$ grains and can vary depending on the fabrication process.

For 2D $(\text{BA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$ films, we did not observe such a transition process from electronic to ionic conductivity when the temperature was increased to 330 K for the films both in the dark and under illumination. A constant slope was observed with an activation energy of 41 ± 7 meV, which should be in the range for electronic conduction. This result well confirms the suppression of ion migration up to 330 K in 2D perovskite films. We believe that organic spacing layers in 2D perovskites should cause the absence of notable ion migration, while it is not clear yet whether there is contribution from the special geometry of grain boundaries in 2D perovskite films.

The absence of obvious ion migration in 2D perovskites should impact the device efficiency and stability. The ion migration-related phenomena, including photocurrent hysteresis, such as switchable photovoltaics,¹¹ photoinduced poling effect,¹² light-induced phase separation,¹³ giant dielectric constant,¹⁴ and self-healing,¹⁵ will be unlikely to occur. It will also alleviate the ion migration-related degradation process. The ion migration in 3D perovskite devices can accelerate the decomposition of perovskite films, create defects as nonradiative recombination centers, and cause degradation of charge transport layers and corrosion of metal electrodes. Apart from the enhanced moisture resistance introduced by the hydrophobicity of the long BA cation chain, we speculate that the moisture and oxygen ingress in low-dimensional perovskite films may be also suppressed because of the suppression, which contributes to the enhancement of stability of the devices based on these materials.

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Notes

The authors declare no competing financial interest.

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