

Atomistic origins of the preferential stabilization of perovskite over non-perovskite phases of mixed cation lead halide perovskites

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Mixed cation lead halide perovskites have attracted wide attention due to the possibility of preferentially stabilizing the perovskite phase with respect to photovoltaically less suitable competing phases.[1-2] In this work, through a theoretical analysis, we study the phase stability of binary $\text{HC}(\text{NH}_2)_2^+$ (FA^+)-rich[1] and Cs^+ -rich FA/Cs and CH_6N_3^+ (GUA)/ FA mixtures as well as ternary $\text{Cs}/\text{GUA}/\text{FA}$ mixtures. Our study yields a series of design principles for the fabrication of stable lead halide perovskites with mixtures of monovalent cations.

Calculations of FA^+ -rich $\text{Cs}_x\text{FA}_{(1-x)}\text{PbI}_3$ ($0 < x < 0.5$),[1] suggest that if the structural characteristics of the non-perovskite δ phases of the pure compounds differ significantly, mixing is energetically favoring the perovskite over the non-perovskite phase. However, despite the significant differences in the δ phases of FAPbI_3 and CsPbI_3 , in Cs^+ -rich $\text{FA}_x\text{Cs}_{(1-x)}\text{PbI}_3$ ($0 < x < 0.5$) mixtures, stable perovskite phases cannot be formed. This contrasting finding leads us to consider not only the structural differences between the non-perovskite phases of the pure compounds but also the volume difference between their perovskite phases. Indeed, mixing in the perovskite phase is getting unfavorable upon incorporation of a large cation into a relatively small lattice.

Although mixing of FA/GUA is possible, it is not sufficient to stabilize the perovskite phase at room temperature. Probing the possible stabilization in ternary $\text{Cs}/\text{GUA}/\text{FA}$ mixtures, instead we conclude that stable mixtures that contain 17% of Cs^+ and GUA up to 33% can be formed. This finding reveals a third design principle, according to which mixing monovalent cations that would be per se outside the stability range with other cations that can compensate the size, so that the average radii of the mixed cations lies within the suitable Goldschmidt tolerance range[3] can lead to the formation of ternary perovskite mixtures with enhanced stability.

Our investigations on the potential preferential stabilization of the perovskite phase upon mixing is complemented by band gap calculations of the mixtures that show that the stable perovskite phases of binary FA^+ -rich FA/Cs and of the ternary $\text{Cs}/\text{GUA}/\text{FA}$ mixtures can be potential candidates for single-junction solar cell applications. In addition, if the perovskite phase of Cs^+ -rich Cs/FA mixtures could be kinetically trapped it would be a potential candidate for tandem solar cell applications. In such a way, our suggested design principles pave the way for the preparation of mixed cation lead halide perovskites with enhanced stability and optical properties.

References

1. C. Yi, J. Luo, S. Meloni, A. Boziki, N. Ashari-Astani, C. Grätzel, S. M. Zakeeruddin, U. Rothlisberger and M. Grätzel, *Energy Environ. Sci.* **9** (2016), 656.
2. M. Saliba, T. Matsui, K. Domanski, J.-Y. Seo, A. Ummadisingu, S. M. Zakeeruddin, J.-P. Correa-Baena, W. R. Tress, A. Abate, A. Hagfeldt and Michael Grätzel, *Science* **354** (2016), 206.
3. V. M. Goldschmidt, *Sci. Nat.* **14** (1926), 477.