

Alloying Large Organic Cations into the Perovskite Framework for Enhanced Thermal Stability and Transport Properties

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The studies on the organic–inorganic hybrid perovskites has attracted enormous attention in the past few years. However, these studies are majorly focused on hybrid perovskites hosting with a limited number of small organic cations, such as methylammonium (MA) and formamidinium. Such materials appear as semiconductors with excellent charge transport properties due to the easy fitting of these small cations into the perovskites three-dimensional (3D) lead halide framework. Up-to-now, the studies on the role of the incorporation of larger cations, such as ethylammonium (EA), into the perovskites framework remain largely unexplored. Here we show for the first time that ethylammonium can in fact be incorporated coordinately with methylammonium in the lattice of a 3D perovskite, accompanied by lattice strains. In Figure 1a, we investigated the phase transition of $\text{EA}_{0.17}\text{MA}_{0.83}\text{PbI}_3$ by temperature-dependent XRD, which clearly demonstrated a tetragonal–cubic phase transition roughly at -30°C , much lower than that of MAPbI_3 (ca. 57°C). This phenomenon suggests a lower free energy and higher stability in $\text{EA}_{0.17}\text{MA}_{0.83}\text{PbI}_3$ crystal. In addition, we annealed MAPbI_3 thin films with and without EA at 85°C for 24 h in N_2 . We found in Figure 1b that the EA containing film has much less PbI_2 decomposed from perovskites due to the enhanced thermal stability. We thus conclude that the inclusion of EA cations largely improved the stability of perovskites framework. More importantly, such structural modification markedly enhanced the charge carrier lifetime. Generally, the crystal engineering strategy employed in this work greatly broadens the choices of organic cations for 3D perovskites, opening up new degrees of freedom to tailor their optoelectronic and environmental properties.

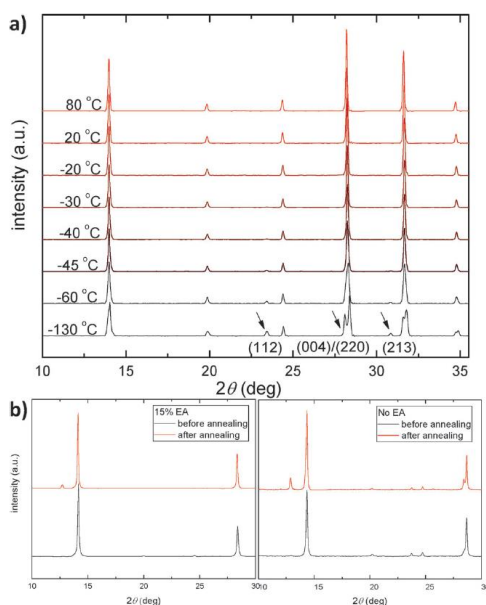


Figure 1. a) Temperature-dependent XRD patterns of $\text{EA}_{0.17}\text{MA}_{0.83}\text{PbI}_3$ crystal powders examined from -130 to 80°C . b) XRD patterns of MAPbI_3 (without EA) and $\text{EA}_{0.17}\text{MA}_{0.83}\text{PbI}_3$ (with EA) thin films before and after 24 h annealing at 85°C .