Cesium Distribution in Perovskites revealed by ^{127}I NQR

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Formamidinium-based hybrid lead iodide perovskites ($FAPbI_3$) have recently led to significant improvements in the performance of perovskite photovoltaics. One of the remaining major hurdles is the instability of the black α-$FAPbI_3$, which undergoes a phase transition from the desired three-dimensional cubic perovskite phase to a non-perovskite one-dimensional hexagonal lattice. Partial substitution of FA with Cs is known to stabilize the material's cubic perovskite structure, as shown by X-ray diffraction. We address this problem by ^{127}I nuclear quadrupole resonance (NQR), which has been shown to be able to resolve structural changes with accuracies commensurate with synchrotron X-ray diffraction and scattering.[1] We report the ^{127}I NQR spectra of $FA_{1-x}Cs_xPbI_3$ (x = 0 - 0.1) crystals showing not only the averaged but all the local iodide structures.[2] Already minute quantities of Cs ions drastically change the observed ^{127}I NQR spectra. 5% of cesium ion incorporation leads to immense inhomogeneous line broadening and an additional species observable at lower frequencies. This new species could be assigned to iodide environments with one of the four FA neighbours being replaced by Cs, showing reduced quadrupolar coupling constants and increased asymmetry. For higher amounts of ion substitution, iodide environments with two cesium neighbours can be observed. This species is highly overrepresented with respect to a homogeneous halide distribution. This could be attributed to cesium clustering, foreshadowing the complete phase segregation occurring upon further cesium addition. These findings showcase the great potential of halide NQR for characterizing local structures of perovskite-based materials, enabling improved models for property calculations, as well as allowing for a better atomic picture of these complex materials.

[1] Piveteau L., *et al., ACS Cent. Sci.* **2020**, 6, 7, 1138–1149.
[2] Aebli, M., Porenta N., Aregger N., Kovalenko M.V., *Chem. Mater.* **2021**, 33, 17, 6965–6973.