Uncovering Halide Mixing and Octahedral Dynamics in Cs_2SnX_6 by Multinuclear Magnetic Resonance Spectroscopy

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Cs_2SnX_6 (X = Cl, Br, I) have emerged as promising lead-free and ambient-stable materials for photovoltaic and optoelectronic applications. To advance these promising materials, it is crucial to determine the correlations between physical properties and their local structure and dynamics. Solid-state NMR spectroscopy of multiple NMR-active nuclei (^{133}Cs, ^{119}Sn and ^{35}Cl) in these cesium tin(IV) halides has been used to decode the structure, which plays a key role in the materials' optical properties. The ^{119}Sn NMR chemical shifts span approximately 4000 ppm and the ^{119}Sn spin-lattice relaxation times span three orders of magnitude when the halogen goes from chlorine to iodine in these diamagnetic compounds. Moreover, ultrawideline ^{35}Cl NMR spectroscopy for Cs_2SnCl_6 indicates an axially symmetric chlorine electric field gradient tensor with a large quadrupolar coupling constant of ca. 32 MHz, suggesting a chlorine that is directly attached to Sn(IV) ions. Variable-temperature ^{119}Sn spin lattice relaxation time measurements uncover the presence of hidden dynamics of octahedral SnI_6 units in Cs_2SnI_6 with a low activation energy barrier of 12.45 kJ/mol (0.129 eV). We further show that complete mixed-halide solid solutions of $Cs_2SnCl_xBr_{6-x}$ and $Cs_2SnBr_xI_{6-x}$ ($0 <= x <= 6$) form at any halogen compositional ratio. ^{119}Sn and ^{133}Cs NMR spectroscopy resolve the unique local $SnCl_nBr_{6-n}$ and $SnBr_nI_{6-n}$ ($n = 0–6$) octahedral and $CsBr_mI_{12-m}$ ($m = 0–12$) cuboctahedral environments in the mixed-halide samples. The experimentally observed ^{119}Sn NMR results are consistent with magnetic shielding parameters obtained by density functional theory computations that were obtained to model the random halogen distribution in mixed-halide analogues. Finally, we demonstrate the difference in the local structures and optical absorption properties of Cs_2SnI_6 samples prepared by solvent-assisted and solvent-free synthesis routes.