Stability Enhancement and Optoelectronic Tailoring of Lead-Free $CsSnX_3$ and Cs_2SnX_6 Halides through Anion-Anion Exchange

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The perovskite $CsSnX_3$ and defect-perovskite Cs_2SnX_6 (X = I, Br, Cl) systems are prominent lead-free candidates for next-generation optoelectronic applications, yet they are limited by distinct fundamental factors. While the substitution of toxic lead with tin facilitates industrial viability, $CsSnX_3$ halides exhibit poor chemical stability due to the spontaneous oxidation of tin from the Sn^{2+} state to the more stable Sn^{4+} state. Cs_2SnX_6 compounds demonstrate superior moisture resistance as tin is already present in the Sn^{4+} oxidation state, they lack the extensive three-dimensional electronic connectivity characteristic of the $CsSnX_3$ perovskite framework.

This study addresses these challenges through compositional engineering via the formation of mixed $Cs_2SnX_{6-x}Y_x$ and $CsSnX_{3-x}Y_x$ solid solutions. First-principles DFT calculations indicate that replacing iodine with more electronegative bromine or chlorine significantly enhances thermodynamic stability. Specifically, the formation energy of Cs_2SnX_6 increases from 33.44 eV (for X = I) to 55.11 eV (for X = Cl). Analysis of the mechanical properties shows that $CsSnX_3$ possess higher structural rigidity, with $CsSnCl_3$ reaching a maximum bulk modulus of 20.6 GPa. Furthermore, the E_g band remains highly tunable. The primary mechanism underlying these improvements involves the modification of the electronic density of states (DOS) and the halide-induced "size effect." The substitution of large I atoms with smaller Br or Cl anions triggers unit-cell contraction and a corresponding reduction in Sn–X and Cs–X bond lengths. DOS analysis reveals that increasing halide electronegativity shifts the hybridized X p-states toward lower energy levels, thereby widening the band gap and increasing the covalent character of the chemical bonding. These electronic shifts directly correlate with the observed gains in thermodynamic and structural integrity. To limit phase separation in mixed-halide systems, a synthesis approach utilizing hydriodic acid (HI) is proposed to facilitate the stable incorporation of iodide into Cs_2SnCl_6 matrices. These optimized materials are highly suitable for high-efficiency solar cells, light-emitting diodes (LEDs), photodetectors, and hole-transporting layers in dye-sensitized photovoltaics.