Electronic Supplementary Material (ESI) for RSC Advances.

Fluorine Ion Induced Phase Evolution of Tin-based Perovskite Thin Films: Structure and Properties

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Supporting information available:

1. Schematic illustration of the evaporation method

2. Supercells and F doping models of B-γ-$CsSnI_3$

3. Density of Localized Trapped Charge

Schematic illustration of the evaporation method

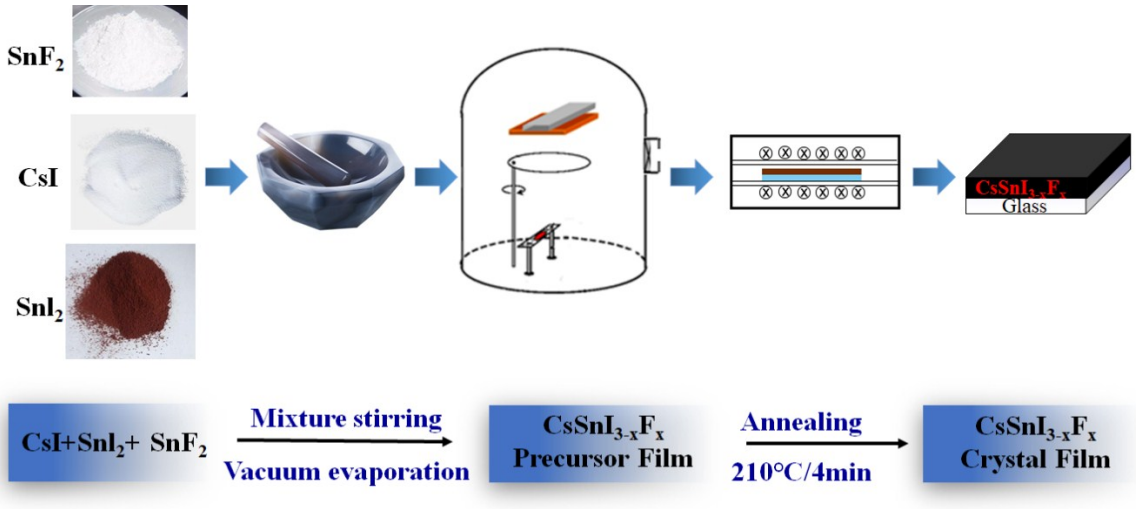

Fig.S1. Schematic illustration of the evaporation method.

To better understand of the role of F on the improved stability of $CsSnI_{3-x}F_x$ films, we decided to explore density functional theory (DFT) simulation using Vienna ab initio simulation package (VASP).

Supercells and F doping models of B-γ-$CsSnI_3$

B-γ-$CsSnI_3$ has 20 atoms and exhibits an orthorhombic structure with the *Pnma* space group symmetry. The supercells and F doping models corresponding to the minimum energy was identified as the computational model. Within the two supercells, the minimum energy of F doping models formed from the supercell A, and there are two doping positions: the horizontal and vertical positions.

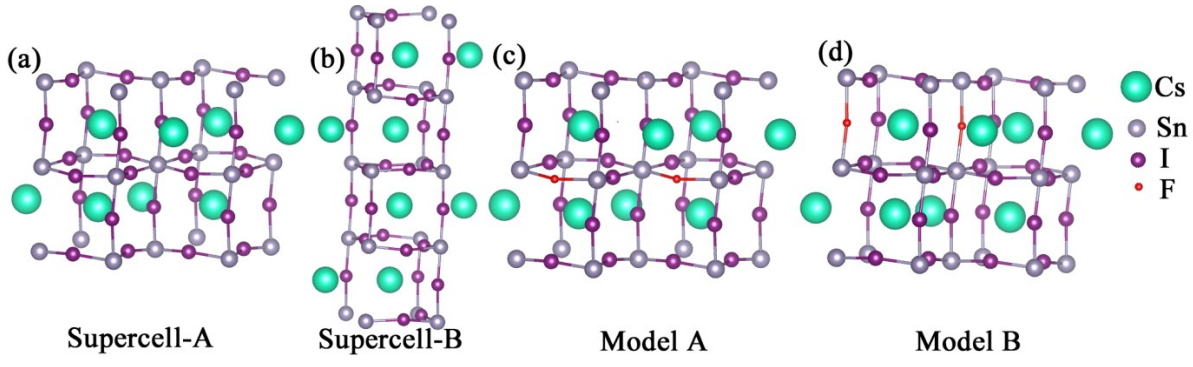

Fig.S2. Supercells and F doping models of B-γ-$CsSnI_3$, Cs is in green, Sn is in gray, the I anions are purple, and F is red.

Density of Localized Trapped Charge

The part of the content is quoted here: the local charge density in order to reveal the characteristics of bonding in the $CsSnI_{3-x}F_x$ films. Fig.S2 further presented the local charge density of B-γ-$CsSnI_{3-x}F_x$ films unit cells which x = 0, 1, 2 and 3. F-Sn-I clusters are more electronegative than I-Sn clusters because of that fluorine has strong electron binding ability. With the increase of fluorine content, Sn-I-Sn structure tends to I-Sn structure, that is to identify I turns from bidirectional to unidirectional, which explains the transition of Sn^{2+} to Sn^{4+} valence. It is clear shown that doping only plays a role of local stability. Thus, it is proven that the phase transition time is slowed down, not stopped. These results are consistent with our assumptions in **Introduction**.

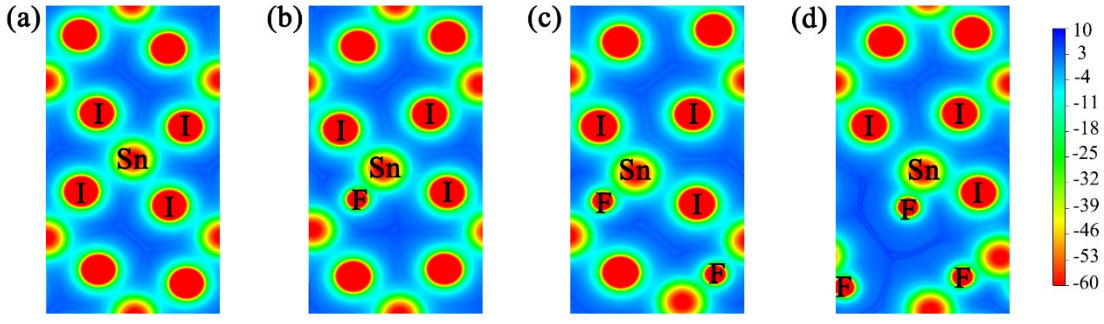

Fig.S3. Electron Localization Function for B-γ-$CsSnI_{3-x}F_x$ where x = 0, 1, 2 and 3. Blue regions are domains of high electron localization while red regions are domains of low electron localization.