Supplementary Information (SI) for Journal of Materials Chemistry A.
This journal is © The Royal Society of Chemistry 2025

Supplemental Material

Enhanced negative electrocaloric effect in Sn-doped $PbHfO_3$ films through phase transition induction

Yongqing Zhao[a], Wenhua Li[a,*], Xingui Tang[a], Zhifei Jian[a], Lin Zhang[a], Xi Zhu[a], Yongxi Liang[a], Yanping Jiang[a], Xiaobin Guo[a] and Kai Yan[b]

[a]*Guangdong Provincial Key Laboratory of Sensing Physics and System Integration Applications, School of Physics and Optoelectronic Engineering, Guangdong University of Technology, Guangzhou Higher Education Mega Center, Guangzhou 510006, People's Republic of China*

[b]*Analysis and Test Center of Guangdong University of technology, Guangzhou 510006, People's Republic of China*

* Corresponding author.

E-mail address: liwenhuat@gdut.edu.cn (W. Li).

Fig. S1 Flow chart of PHS-100*x* films preparation by sol-gel method.

Initially, hafnium acetylacetonate ($Hf(CH_3COCHCOCH_3)_4$, 97%) was dissolved in a mixed solution of glacial acetic acid (CH_3COOH) and ethylene glycol monomethyl ether ($C_3H_8O_2$) under heating until complete dissolution. Subsequently, lead acetate trihydrate ($Pb(CH_3COO)_2$, 99.5%) and tin tetrachloride pentahydrate ($SnCl_4 \cdot 5H_2O$, 99.0%) were mixed and dissolved in ethylene glycol methyl ether ($C_3H_8O_2$). After this solution cooled, the hafnium acetylacetonate ($Hf(CH_3COCHCOCH_3)_4$, 97%) solution was added. Finally, a small amount of acetylacetone ($C_5H_8O_2$) was added to the mixed solution as a stabilizer, and it was stirred using a magnetic stirrer. A clear PHS-100*x* solution, free of precipitation and with a concentration of 0.2 mol/L, was obtained after 40 minutes of stirring. To preclude potential errors in the preparation of film components arising from lead loss during the solution preparation stage, it is imperative to ensure that the lead acetate trihydrate ($Pb(CH_3COO)_2$) addition exceeds 10% during solution configuration. Following an aging period of 3 days, the precursor solution achieved the requisite stability and uniformity, which is critical for the formation of crack-free films during the subsequent annealing process. Ultimately, the prepared PHS-100*x* solution was dropped onto the center of the FTO/glass. Spin-coating was performed at a low speed of 800 rpm for 10 s, followed by a high speed of 3000 rpm

for 20 s. The resulting coating underwent 10 repeated cycles, each comprising a 5 min pyrolysis at 200°C and a 15 min sintering at 400°C, followed by annealing at 650°C for 15 min. To facilitate subsequent film testing, gold electrodes were sputtered onto the films using magnetron sputtering for a duration of 110 seconds.

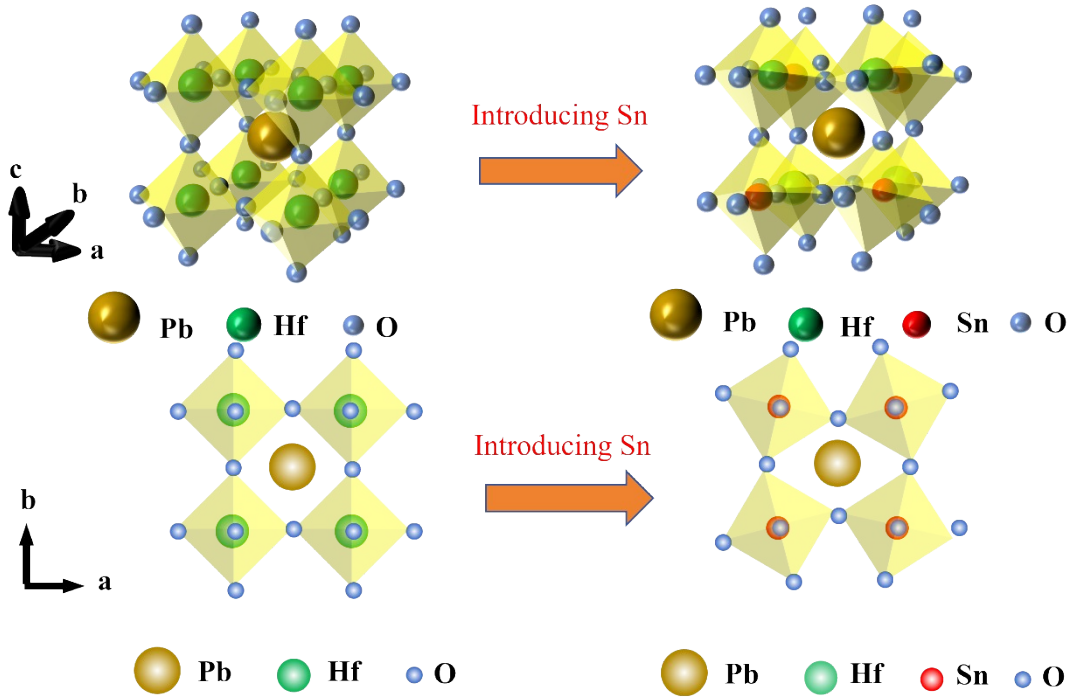

Fig.S2 Schematic of $PbHfO_3$ Crystal Structure.

Table S1. Interplanar spacing (d) for different Sn^{4+} doping concentrations

concentration of Sn^{4+} (%)	2θ (°)	θ (°)	sinθ	***d*** **(Å)**
0.0	54.24	27.12	0.455823	**1.69150**
0.5	54.26	27.13	0.455876	**1.69142**
1.0	54.29	27.145	0.455982	**1.69126**
2.0	54.34	27.17	0.456088	**1.69084**

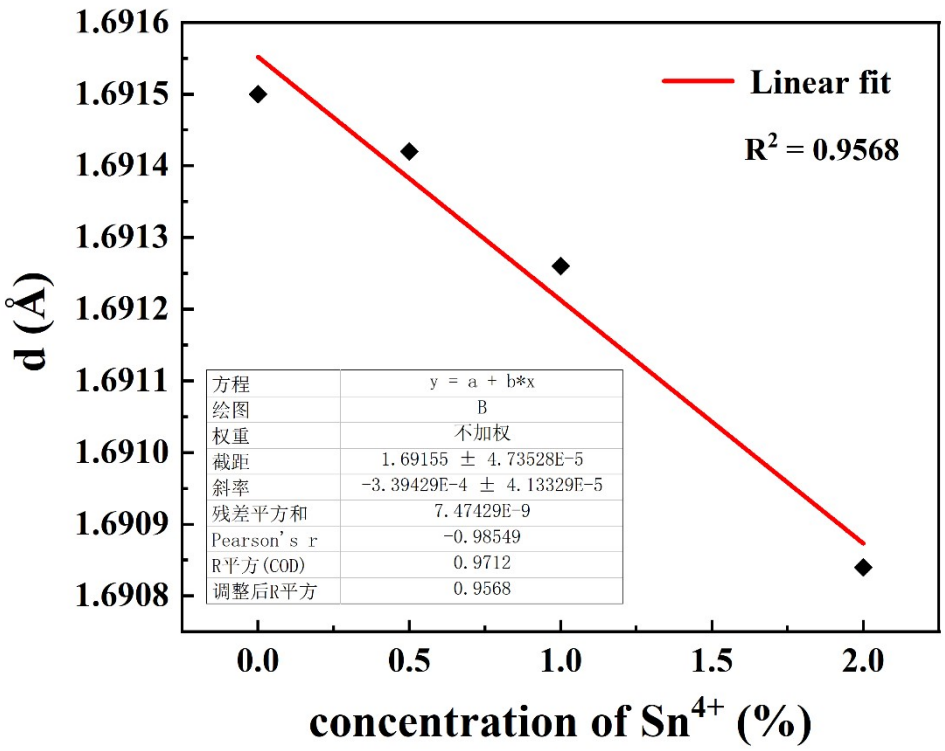

Fig. S3 Interplanar spacing (*d*) versus Sn^{4+} ion concentration with linear fit.