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Electronic Supplementary Information

Tuning the Luminescent Properties of a Three-Dimensional Perovskite Ferroelectric (Me-Hdabco)CsI_3 Via doping Sn(II)

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1、Synthesis

Synthesis of (Me-Hdabco)CsI_3: A mixture of Me-dabco (10 mmol, 2.54 g) (Me-dabco = N-methyl-1,4-Diazabicyclo[2.2.2]octane), CsI (10 mmol, 2.60 g), HI (47%, 10 mmol, 5.44 g), and H_3PO_2 (1 mL) in 20 mL aqueous solution until a clear solution was formed. And the mixture solution was evaporated slowly at 303 K. After 3 days, the colorless and transparent bulk single-crystal of (Me-Hdabco)CsI_3(**1**) was synthesized at the bottom of the beaker, (Yield: 5.45 g, 85% based on Cs). The purity was confirmed by powder X-ray diffraction (PXRD).

Synthesis of Sn-doping crystal: The Sn-doping crystal was synthesized by the similar conditions as **1**. For the detail for synthesis of Sn-doped samples: different Sn(II)-feeding concentrations of SnI_2 (1% Sn, 0.1 mmol; 5% Sn, 0.5 mmol; 10% Sn, 1 mmol; 20% Sn, 2 mmol) was added to the mixed solution of Me-dabco (10 mmol, 2.54 g) (Me-dabco = *N*-methyl-1,4-Diazabicyclo[2.2.2]octane), CsI (10 mmol, 2.60 g), HI (47%, 10 mmol, 5.44 g), and H_3PO_2 (1 mL) and 20 mL deionized water, and then stirred until completely dissolved of SnI_2. The mixed solution is filtered and after three days, colorless strip crystals tin-doping crystal were grown at the bottom of the beaker. And the rest Sn-doped crystals only need to be adjusted according to the doping amount.

2、Measurement and Methods

2.1 Crystal Structure Determination

All single-crystal X-ray diffraction data were collected on a Rigaku synergistic diffractometer with Mo-Kα (λ = 0.71073 Å) radiation from a graphite monochromator, and the crystal structure were solved using the direct method and refined based on the least square method by the Olex2 software equipped with ShelXL programs.

2.2 PXRD Measurements

Powder X-ray diffraction patterns were recorded on a Rigaku DMax 2500 powder diffractometer. Measurement angle ranges from 5° to 50° with step size of 0.02° and

scanning speed 2°/min.

2.3 Variable-temperature Dielectric Permittivity Measurement

The dielectric measurements were carried on Tonghui TH2828A impedance analyzer. Silver conducting paste deposited on the plate surfaces was used as electrodes on pressed-powder pellets.

2.4 Differential Scanning Calorimetry (DSC) measurement

Differential scanning calorimetry (DSC) measurement was performed using a Netzsch differential scanning calorimetry 214 Polyma under nitrogen atmosphere at atmospheric pressure, and the heating-cooling rate is 20 K min^{-1}.

The calculation of ΔS and N for **1**.

$$\Delta S = \int_{T_2}^{T_1} \frac{Q}{T} dT \approx \frac{\Delta H}{Tc} = 8.784$$

J mol^{-1} K^{-1}

$$N = \exp\left(\frac{\Delta S}{R}\right) = 2.877$$

2.5 TG Measurement

Thermogravimetry (TG) analyses were recorded on a NETZSCH STA 449F3 instrument in the temperature range from 300 K to 900 K with a heating rate of 10 K·min^{-1} under a dry N_2 atmosphere.

2.6 Photoluminescence Properties Measurement

Steady-state PL emission and PL excitation (PLE) spectra were measured using a PL spectrometer (FLS980; Edinburgh Instruments). Temperature-dependent steady-state and TRPL spectra were recorded by using a FLS980 spectrometer (Edinburgh) equipped with a continuous xenon lamp (450 W), a pulsed flash lamp, and a 375 nm picosecond pulsed laser. The absolute PL quantum yields (QYs) of single crystals were measured by using a standard BaSO4-coated integrating sphere (150 mm diameter, Edinburgh) as the sample chamber mounted on a FLS980 spectrometer.

2.7 SHG Measurement

The SHG measurement were performed by an unexpanded laser beam with low divergence in the temperature range from 300 K to 475 K. The instrument model is Ins 1210058, INSTEC Instruments and the laser is Vibrant 355 II, OPOTEK.

2.8 PFM Measurement

Preparation of thin film samples for (Me-Hdabco)CsI_3 and Sn(II): (Me-Hdabco)CsI_3 at 10% Sn(II)-feeding concentration:100 mg crystal sample was dissolved in 1 mL deionized water, then 20 uL was dropped onto ITO glass and slowly volatilized at room temperature to obtain the thin film samples of (Me-Hdabco)CsI_3 and 10% Sn(II): (Me-Hdabco)CsI_3.

Nanoscale polarization imaging and local switching spectroscopy were carried out using a resonant-enhanced piezoresponse force microscopy (MFP-3D, Asylum Research) on single-crystal film sample. Conductive Pt/Ir-coated silicon probes (EFM-50, Nanoworld) were used for domain imaging and polarization switching studies. To verify the piezoresponse, we applied a 10 V AC driving voltage on the sample to measure the normal and shear responses, with the AC frequency set at the second resonant peak of cantilever-sample system to enhance the sensitivity. The measurement was carried out on the single-crystal slices. To obtain a domain structure, the sample was heated to about 460 K, and then cooled slowly.

2.9 XPS and EDS Measurement

XPS measurements were performed on ESCALAB 250Xi. The EDS measurements were performed on American EDAX Oribis Micobeam X-ray Fluorescence Spectrometer Micro XRF.

2、Supporting Figures

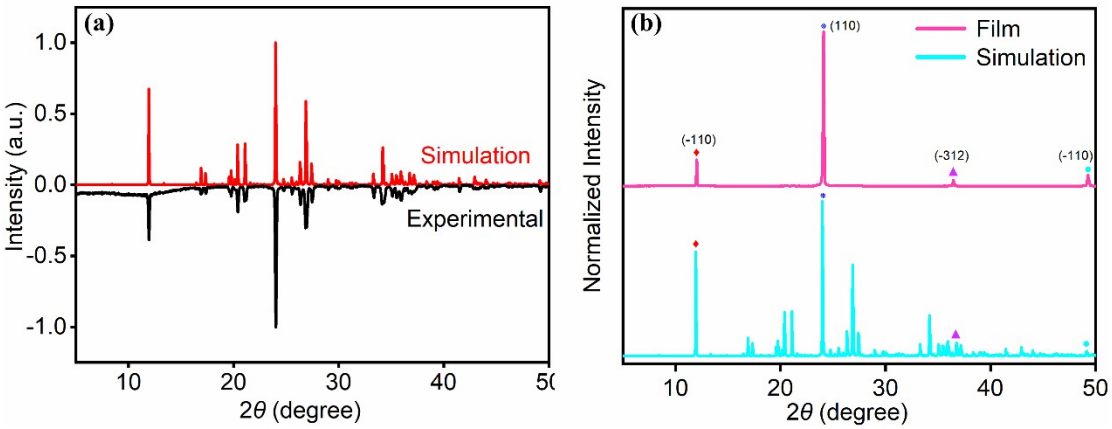


Fig. S1 PXRD patterns of (Me-Hdabco)CsI_3 compared with that simulated one from single crystal X-ray structures, (a) crystal sample and (b) the film sample.

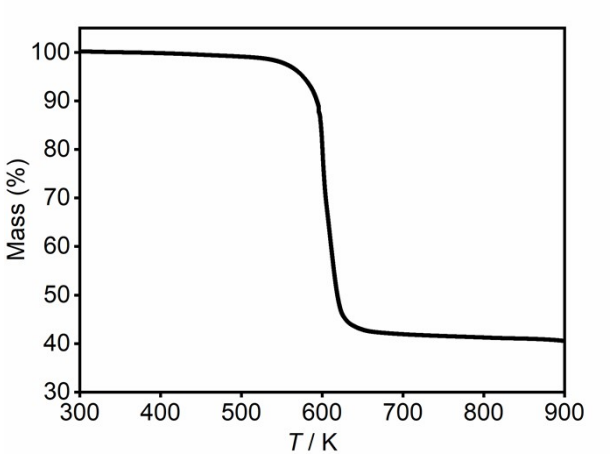


Fig. S2 The TG curve of (Me-Hdabco)CsI_3 (**1**).

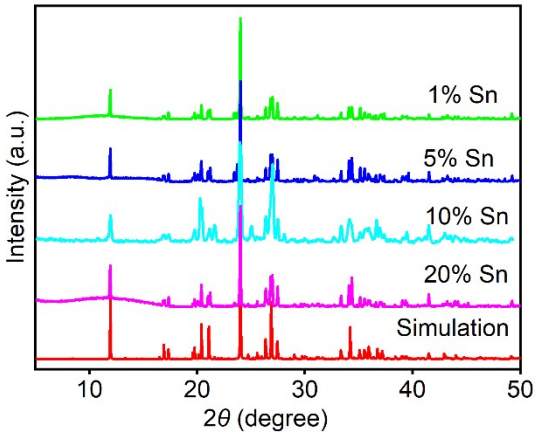


Fig. S3 PXRD patterns of Sn(II): (Me-Hdabco)$CsI_3$with different Sn(II)-feeding concentrations.

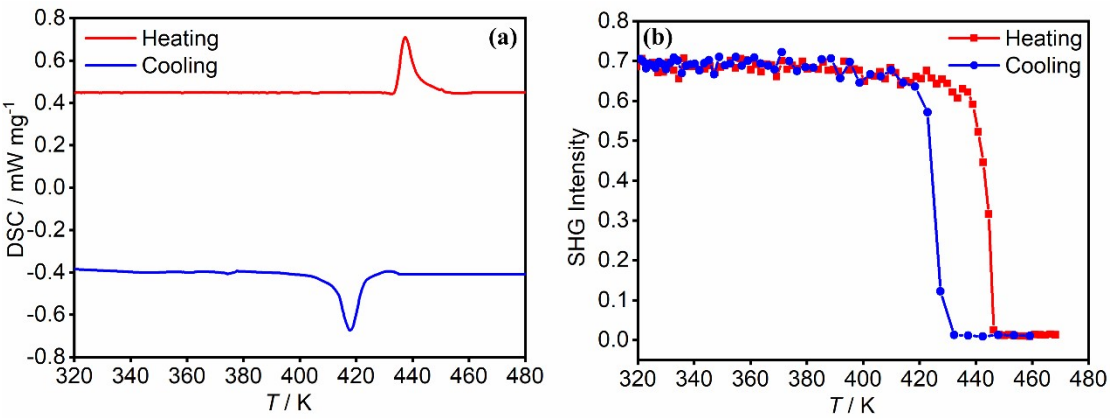


Fig. S4 Symmetry-breaking phase transition in 10% Sn(II):(Me-Hdabco)CsI_3: (a) DSC curves and (b) temperature-dependent SHG response obtained in a heating-cooling cycle.

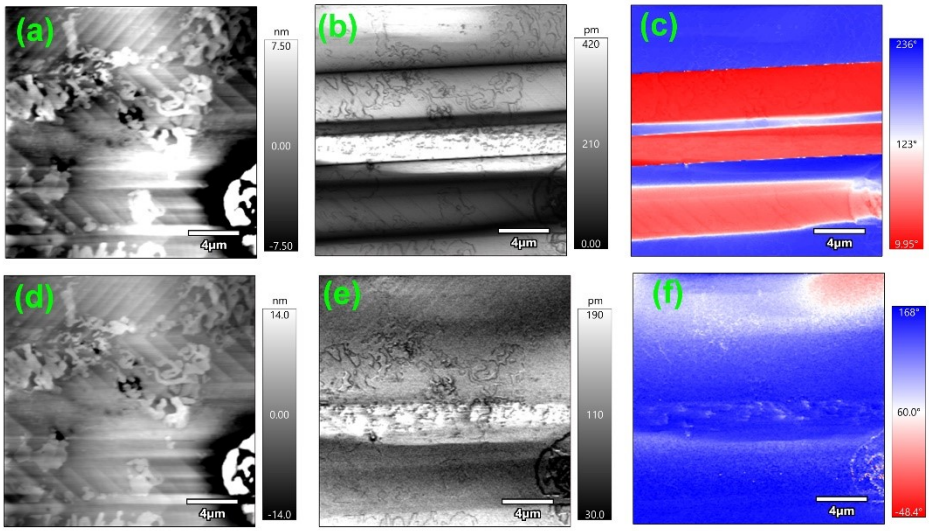


Fig. S5 Domains observed in the as-grown thin film at 10% Sn(II):(Me-Hdabco)CsI_3. Surface topography images (a, d). Vertical and lateral PFM amplitude (b, e) and phase (c, f) images.

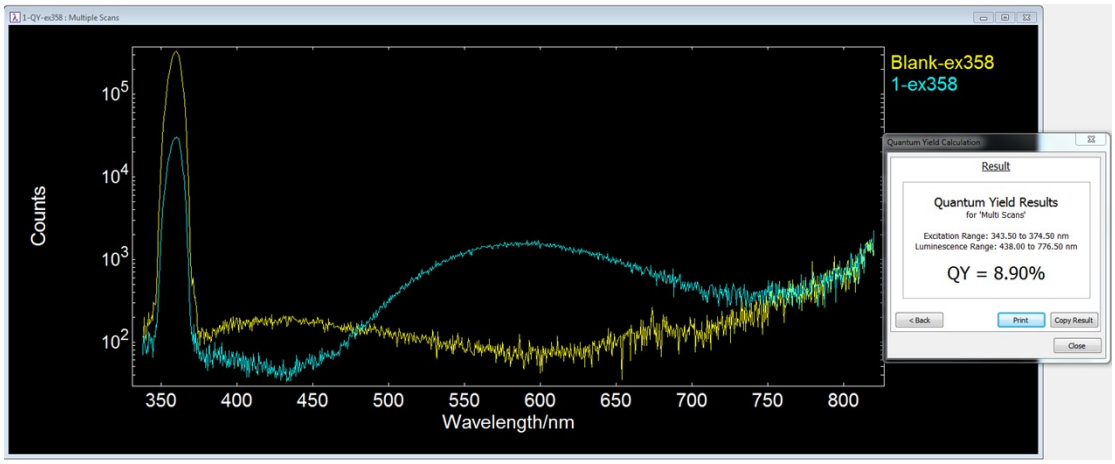
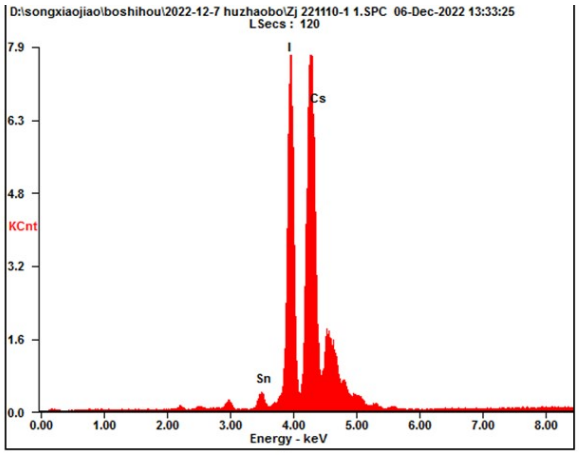


Fig. S6 The fluorescence quantum yield of Sn(II):(Me-Hdabco)CsI_3 with10% Sn(II)-feeding crystal.



Element	*Wt%*	*At%*
SnL	0.81	0.87
I-L	70.72	71.60
CsL	28.47	27.52

Fig. S7 EDX spectrum of 10% Sn(II):(Me-Hdabco)CsI_3.

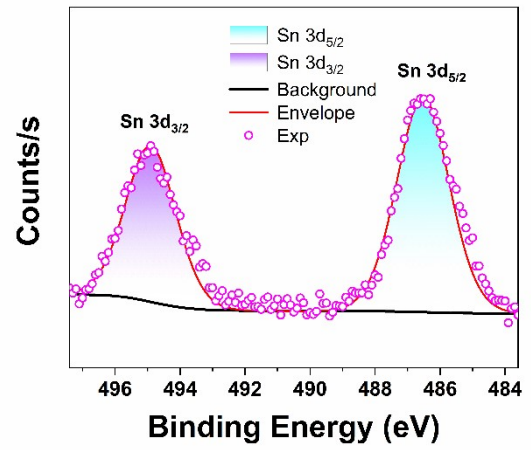


Fig. S8 XPS spectrum of 10% Sn(II):(Me-Hdabco)CsI_3.

3、Supporting Table

Table S1 Crystallographic data and structure refinements of (Me-Hdabco)CsI_3 (**1**).

Temperature / K	**1** at 273 K	**1** at 453 K
Formula	$C_{28}H_{64}N_8Cs_4I_{12}$	$C_4H_9N_2CsI_3$
Formula weight	2567.31	598.74
Crystal system	Monoclinic	Cubic
Space group	*Cc*	$Pm\bar{3}m$
a / Å	20.4211(9)	7.4727(18)
b / Å	21.4617(8)	7.4727(18)
c / Å	14.8276(6)	7.4727(18)
β / °	90.481(3)	90
Volume /Å^3	6498.3(5)	417.3(3)
Z	4	1
ρ_{calc}g/cm^3	2.624	2.383
μ / mm^{-1}	7.953	7.731
F(000)	4576.0	261.0
2*θ*	3.9-58.718	5.452-59.836
Index ranges	-26≦*h*≦23 -29≦*k*≦24 -19≦*l*≦17	-8≦*h*≦9 -9≦*k*≦9 -8≦*l*≦10
Goodness-of-fit on F^2	1.085	1.113
Final *R* indexes [I>=2σ(I)]	R_1 = 0.0527 wR_2 = 0.1507	R_1 = 0.0541 wR_2 = 0.1615
Final *R* indexes [all data]	R_1 = 0.0654 wR_2 = 0.1580	R_1 = 0.0633 wR_2 = 0.1677
Reflections collected	20564	2693
CCDC	2225022	2225021

Table S2 Crystallographic data and structure refinements of Sn(II):(Me-Hdabco)CsI_3 with different Sn^{2+}-feeding.

Temperature / K	5% Sn at 299 K	10% Sn at 299 K	10% Sn at 455 K
Formula	$C_{28}H_{64}N_8Cs_4I_{12}$	$C_{14}H_{28}N_4Cs_2I_6$	$C_7H_{28}N_4CsI_{36}$
Formula weight	2567.31	1279.62	597.67
Crystal system	Monoclinic	Orthorhombic	Cubic
Space group	*Cc*	*Aea*2	$Pm\bar{3}m$
a / Å	20.4486(8)	14.8438(3)	7.4849(5)
b / Å	21.4876(7)	21.4841(4)	7.4849(5)
c / Å	14.8333(4)	20.4535(5)	7.4849(5)
β / °	90	90	90
Volume /Å^3	6517.6(4)	6518.8(2)	419.33(8)
Z	4	8	1
ρ_{calc}g/cm^3	2.616	2.608	2.367
μ / mm^{-1}	7.929	7.927	7.700
F(000)	4576.0	4544.0	256.0
2θ	3.79-62.14	3.792-49.998	5.442-59.43
Index ranges	-27≦*h*≦28 -30≦*k*≦26 -20≦*l*≦20	-17≦*h*≦17 -25≦*k*≦25 -24≦*l*≦24	-8≦*h*≦3 -10≦*k*≦8 -8≦*l*≦9
Goodness-of-fit on F^2	1.073	1.229	1.065
Final *R* indexes [I>=2σ(I)]	R_1 = 0.0527 wR_2 = 0.1411	R_1 = 0.0661 wR_2 = 0.1479	R_1 = 0.0490 wR_2 = 0.1517
Final *R* indexes [all data]	R_1 = 0.0679 wR_2 = 0.1499	R_1 = 0.0685 wR_2 = 0.1489	R_1 = 0.0545 wR_2 = 0.1603
Reflections collected	37930	49215	879
CCDC	2235373	2234582	2235374

Table S3 Cell parameters of Sn doping sample with different Sn^{2+}-feeding.

	1% Sn -phase 1	1% Sn - phase 2	5% Sn- phase 1	5% Sn- phase 2	10% Sn	20% Sn
a / Å	14.8302(7)	20.4551(9)	14.8406(8)	20.4486(8)	14.8438(3)	14.8425(5)
b / Å	21.4697(12)	21.5128(9)	21.4937(9)	21.4876(7)	21.4841(4)	21.5009(9)
c / Å	20.4675(15)	14.8213(7)	20.4532(12)	14.8333(4)	20.4535(5)	20.4308(9)
α / °	90	90	90	90	90	90
β / °	90	90	90	90	90	90
γ / °	90	90	90	90	90	90
V / Å^3	6522.1(15)	6522.1(5)	6524.1(6)	6517.6(4)	6518.8(2))	6520.1(5
Space group	*Aea*2	*Cc*	*Aea*2	*Cc*	*Aea*2	*Aea*2