Supplementary Information for:

Multiferroism in hexagonally stabilized $TmFeO_3$ thin films below 120 K

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Methods

Film Fabrication and Characterizations.

An epitaxial Pt (111) film as the bottom-electrode layer was grown on the Al_2O_3 (0001) substrate using RF magnetron sputtering. A pulsed laser deposition method was then used for the fabrication of a 60-nm-thick hexagonal $TmFeO_3$ (h-TFO) film layer on the Pt(111)/sapphire (Al_2O_3) substrate at a laser energy density of ~1.5 J/cm^2 with the repetition rate of 3 *Hz*. The substrate temperature was held at 850 °C in an oxygen ambience of 200 mtorr. After the PLD growth, a Pt top-electrode layer was deposited to make a capacitor structure.

The temperature-dependent spontaneous polarization was evaluated by measuring the pyrocurrent using a Keithley 487 picoammeter with a sweeping rate of 2 °C /min. Starting at 100 °C, the film was cooled down under an electric poling field of 800 kV/cm along the *c*-axis before measuring the pyroelectric current on heating. *P-E* hysteresis loops with a virtual ground mode were obtained using a Precision LC system (Radiant Technologies, Inc.). Magnetic properties were examined by measuring M-H (SQUID magnetometer, Quantum Design) and M(T) curves (MPMS).

First Principles Calculations

We performed *ab initio* DFT calculations on the basis of the generalized gradient approximation (GGA) and the GGA + U method implemented with the projector augmented wave (PAW)[S1,S2] pseudopotential using the Vienna *ab initio* Simulation Package (VASP).[S3,S4] We adopted (i) a 5×5×3 Monkhorst-Pack ***k***-point mesh centered at Γ,[S5] (ii) a 500eV plane-wave cutoff energy, and (iii) the tetrahedron method with the Blöchl corrections for the Brillouin zone integrations.[S6] The Hubbard U_{eff} of 4.5 eV for Fe was chosen on the basis of previous studies.[S7] We explicitly treated 9 valence electrons for Tm ($5p^6 5d^1 6s^2$), 8 for Fe ($3d^6 4s^2$), and 6 for O ($2s^2 2p^4$). All structural relaxation was performed with a Gaussian broadening of 0.05 eV.[S7] The ferroelectric polarization was calculated using the Berry-phase method.[S8]

Optimized atomic positions in hexagonal $TmFeO_3$

	$P6_3cm$			$P6_3/mmc$		
	x	y	z	x	y	z
Tm1	0	0	0.2766	0	0	0.2500
Tm2	0.3333	0.6667	0.2328	0.3333	0.6667	0.2500
Fe	0.3337	0	0	0.3333	0	0
O1	0.3056	0	0.1664	0.3333	0	0.1667
O2	0.6394	0	0.3370	0.6667	0	0.3333
O3	0	0	0.4770	0	0	0.5000
O4	0.3333	0.6667	0.0209	0.3333	0.6667	0.0000

Table S1. In our density-functional theory (DFT) calculations, the following ground-state lattice parameters at zero pressure were obtained: the hexagonal unit-cell parameters of a = 6.0057 Å and c = 11.6867 Å for $P6_3cm$ phase. Using these parameters, we also computed $P6_3/mmc$ phase.

Computed double-well potential

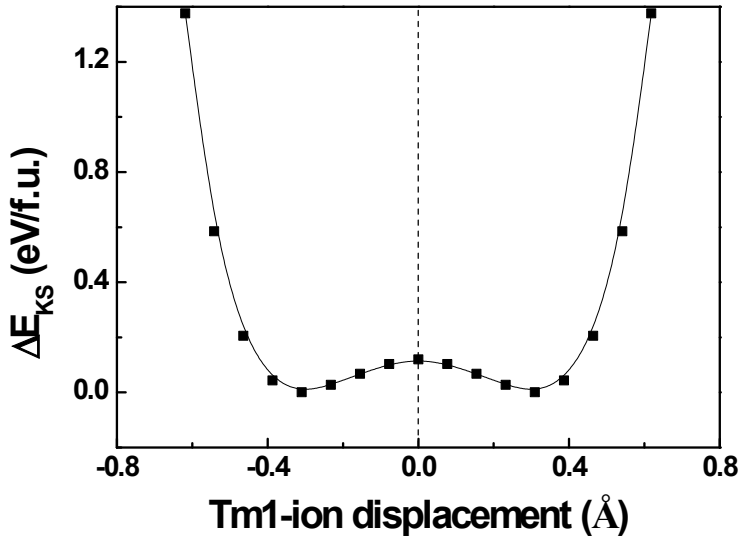

Figure S1. According to the computed double-well potential, the barrier height for the dipole switching along the *c* axis is 0.1198 eV per unit cell. This clearly demonstrates the thermodynamic stability of the ferroelectric $P6_3cm$ phase over the centrosymmetric $P6_3/mmc$ phase. The total Kohn-Sham (KS) energy calculations indicate that the ferroelectric $P6_3cm$ phase is substantially more stable than these phases. According to our density-functional theory (DFT) calculations, the equilibrium off-center displacement of the Tm ion along the c axis is antiparallel to that of the O_A ion but with the same displacement of 0.290Å. This indicates that the net off-centering distortion is 0.580Å.

Local distances between Tm and O ions

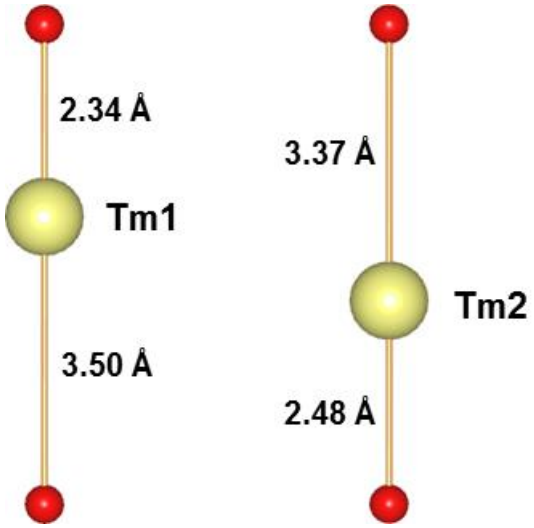

Figure S2. The h-TFO compound possesses two distinct Tm-ion sites in the ferroelectric state. The first dipole (O_A-Tm1-O_A) is antiparallel to the second one (O_A-Tm2-O_A). In addition, the amplitude of the local Tm1 off-centering is larger than that of the local Tm2 off-centering. Thus, the net polarization is parallel to the *c* axis of $P6_3cm$.

Capacitance – Voltage Curves

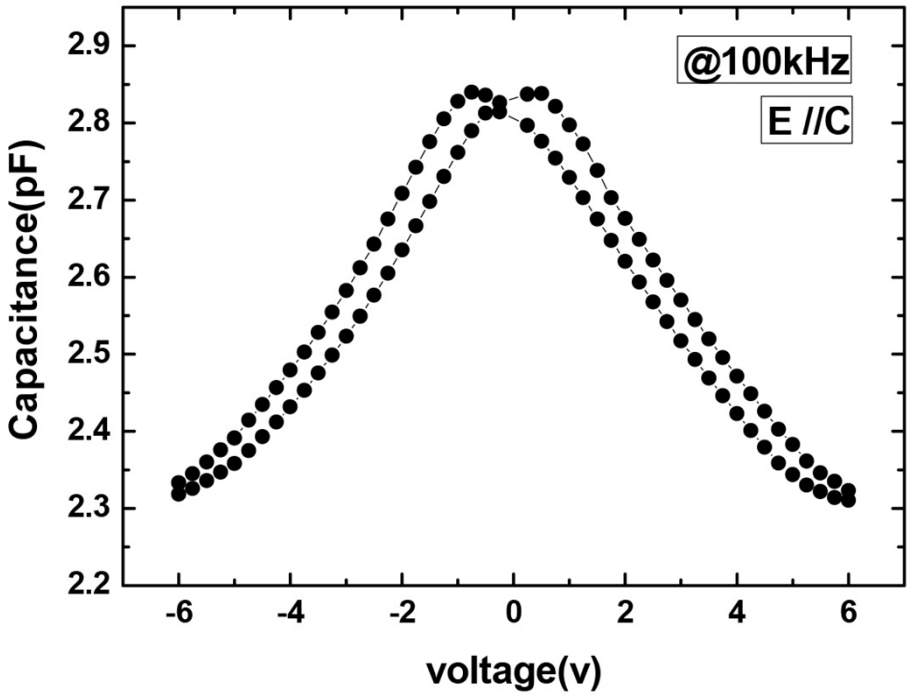

Figure S3. Capacitance-voltage curve of the Pt/h-TFO/Pt capacitor obtained at 100 kHz with the probing electric field parallel to the film-grown direction, [0001]. The ferroelectricity with a non-zero remnant polarization was also confirmed by obtaining a butterfly-shaped hysteresis C-V curve.

Pyroelectric Current Data

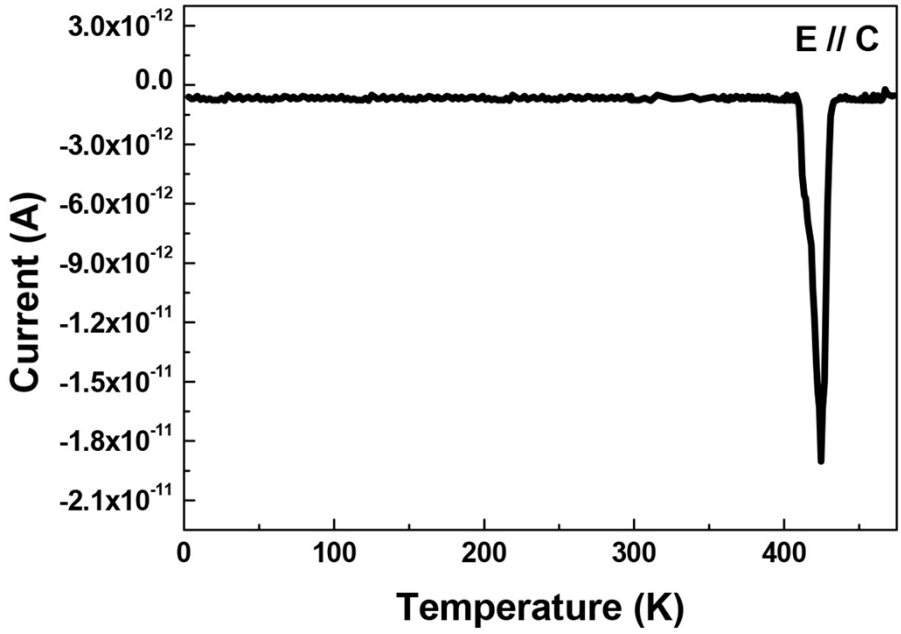

Figure S4. Temperature-dependent pyroelectric current of the h-TFO film obtained using a Keithley 487 picoammeter with a sweeping rate of 2°C/min. The onset of the para-to-ferroelectric transition is observed at ~430 K (Tc, Curie temperature), as described in the main manuscript.

Temperature dependent relative dielectric permittivity curves

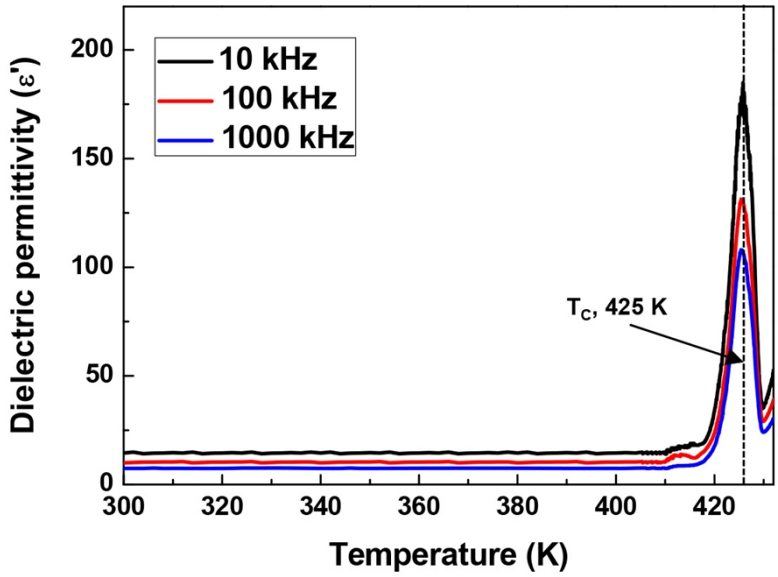

Figure S5. Temperature dependent relative dielectric permittivity curves of the h-TFO film measured at various ac probing frequencies. Note that the peak temperature of the dielectric permittivity coincides well with the onset of the ferroelectric transition at ~430 K.

* References

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