High-Tc Fe-Based Ferroelectric Compound with Large Spontaneous Polarization and Narrow Bandgap

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Experimental Section

Material synthesis and crystal growth

All reagents and solvents in this experiment are reagent grade and can be used without further purification. Add 2 mmol of trimethylpropylammonium bromide and 1 mmol of $FeBr_3$ to a methanol solution (10 mL) containing hydrochloric acid (2 mL). After stirring and dissolving at room temperature, slowly evaporate at 323 K to obtain yellow transparent crystal. In addition, the crystal will not be oxidized or absorb water after being placed in the air for a long time. The PXRD pattern obtained at 298 K matches well with the simulation results of the single crystal structure, showing high crystallinity and phase purity. Elemental analysis, calculated value (%) of **1**: C, 15.09; N, 2.932; H, 3.376. Found: C, 15.11; N, 2.916; H, 3.389.

X-ray diffraction characterization

The single-crystal X-ray diffraction studies were performed with a Bruker Smart Apex II single-crystal diffractometer operating with a graphite-mono-chromated Mo-sealed tube source (Ka radiation, λ= 0.71073 Å). The crystal structure of **1** were determined at 220 K and 400 K. The structures were solved and the models were refined using the SHELXS and SHELXL programs. The data collection and structure refinement of these crystals are summarized in Table S1. The crystallographic information on the crystal structures of **1** determined at 220 K and 400 K had been deposited in CIF format in the Cambridge Crystallographic Database Centre, CCDC: 2262469 and 2262468.

Second-Harmonic Generation

Powder second-harmonic generation (SHG) measurements were carried out by the Kurtz–Perry method. The measurements were performed with a Q-switched Nd: YAG laser at a wavelength of 1064 nm. Polycrystalline **1** sample were ground and sieved into the following particle size ranges: 37-53 μm, 53-75 μm, 75-125 μm, 125-180 μm, and 180-212 μm. All the samples were pressed

between glass slides and secured with tape in 1 mm thick aluminum holders containing an 8 mm diameter hole. They were then placed into a light-tight box and irradiated with the laser of λ = 1064 nm. The intensity of the frequency-doubled output emitted from the samples was collected by a photomultiplier tube. Crystalline KH_2PO_4 (KDP) was also ground and sieved into the same particle size ranges and used as the references.

Piezoelectric microscope (PFM) test

The blue film specially used for mechanical stripping is used to prepare the samples required for PFM test. Cover the blue film on the crystal surface. After compaction for 1 h, tear the blue film off the crystal. A film like chip of compound **1** will be attached to the blue film, and then attach the side of the blue film not attached to the crystal to the ITO conductive glass with silver glue. The test instrument is Asylum Research Atomic Force Microscope (MFP-3D) produced by Oxford Instruments, and the test probe is a silicon conductive probe coated with Pt/Ir.

Instrumentation

The powder X-ray diffraction (PXRD) pattern was performed on the Rigaku D/MAX 2000 PC X-ray diffractometer with Cu radiation (K_{a1} = 1.54060 Å, K_{a2} = 1.54443 Å). The data is collected in the temperature range of 300-420 K during the heating process, and 0 is in the range of 5-50°. The DSC measurement is performed by heating/cooling the powder sample at a rate of 15 K·min^{-1} on the PerkinElmer Diamond DSC instrument. The thermogravimetric analysis (TGA) measurement was performed on the TA-Instruments STD2960 system from room temperature to 800 K in a nitrogen atmosphere at a rate of 10 K·min^{-1}. The dielectric constant of **1** was measured with Agilent or TH2828A impedance analyzer. During the heating and cooling process, the powder particle sample is measured at a rate of 5 K·min^{-1}. The SHG signal was measured by Edinburgh Instruments FLS 920 using a low divergence laser (Nd: YAG, 1064 nm, 5 ns, 1.6 MW peak power, 10 Hz repetition rate). The laser is Vibrant 355 II, OPOTEK. The ferromagnetic hysteresis loop is measured on a standard RT 6000 ferroelectric tester (Albuquerque, USA). The PFM measurement is performed by using the PFM mode on the Asylum MFP-3D infinity atomic force microscope.

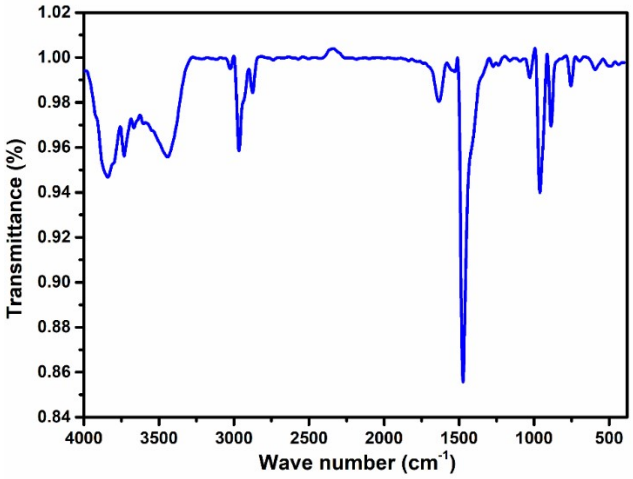

Figure S1 Infrared spectrum of **1.**

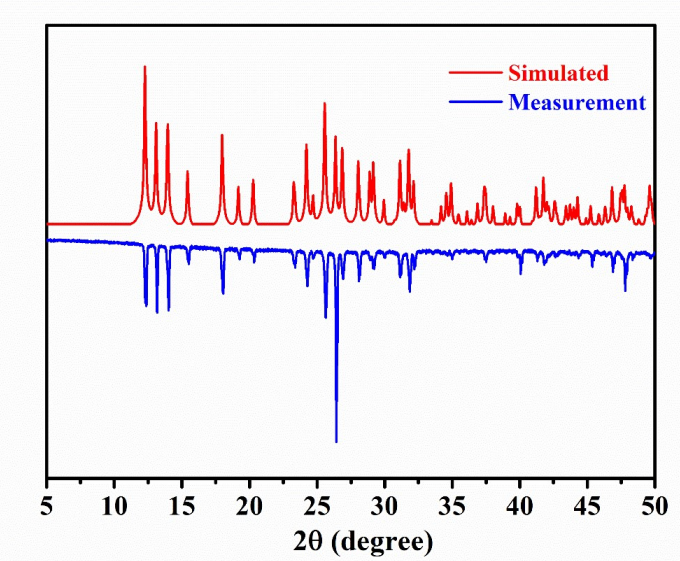

Figure S2. The powder XRD of **1** with the simulated one in red and the measurement in blue.

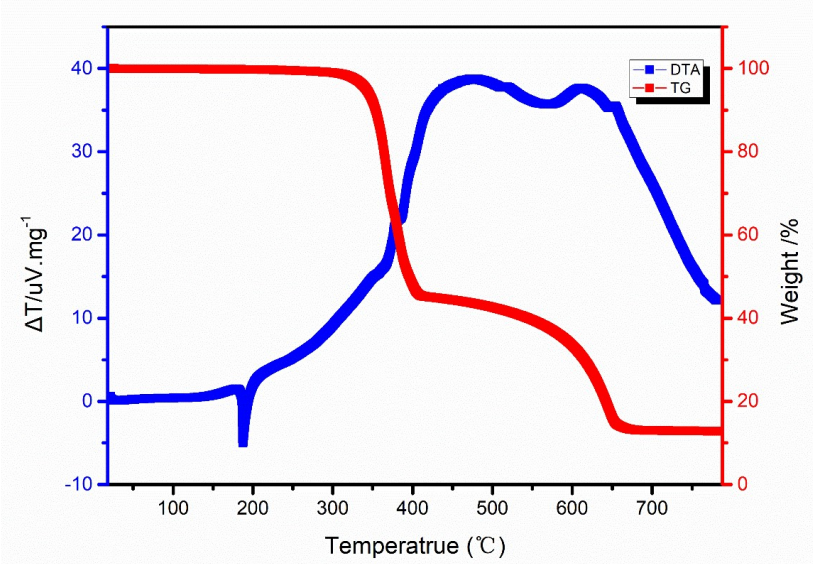

Figure S3 TG diagram for **1**.

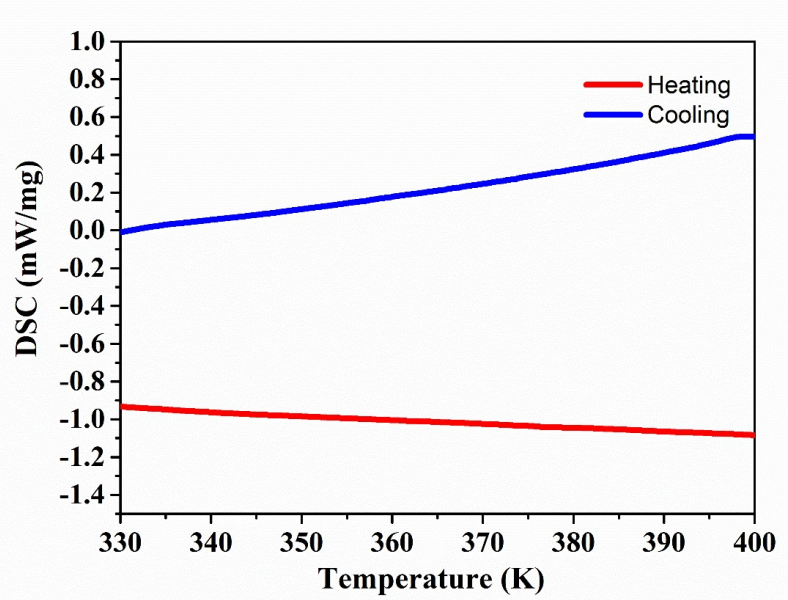

Figure S4. The DSC curve of compound **1**.

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  NELM = 100
  NELMIN = 5
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  EDIFFG = -0.02
  GGA = PE
  ISPIN = 1
  LWAVE = .FALSE.
#----------/Optimize Parameter/----------#
  IBRION = 1
  NSW = 1
  ISIF = 2
  POTIM = 0.3
#----------/Charge Parameter/----------#
  LCHARG = .TRUE.
  LAECHG = .TRUE.
  LREAL = Auto
  ALGO = All
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  SIGMA = 0.05
  ISYM = 0
  LORBIT = 10
```

Figure S5 Parameters for HSE calculation of compound **1**.

Table S1 Crystal data and structure refinement for 1.

Compound	**1-LTP**	**1-HTP**
Empirical formula	$C_6H_{16}Br_4FeN$	$C_6H_{16}Br_4FeN$
Formula weight	477.69	477.69
Temperature/K	219.99(10)	400.0
Crystal system	orthorhombic	orthorhombic
Space group	$Cmc2_1$	$Cmc2_1$
a/Å	8.6868(4)	8.769(3)
b/Å	12.6059(6)	12.709(4)
c/Å	13.3890(6)	13.551(5)
α/°	90	90
β/°	90	90
γ/°	90	90
Volume/Å^3	1466.16(12)	1510.4(9)
Z	4	4
ρ_{calc}g/cm^3	2.164	2.101
μ/mm^{-1}	11.892	11.544
F(000)	900.0	900.0
Final R indexes [I>=2σ (I)]	R_1 = 0.0285, wR_2 = 0.0523	R_1 = 0.0689, wR_2 = 0.1728
Final R indexes [all data]	R_1 = 0.0385, wR_2 = 0.0543	R_1 = 0.1223, wR_2 = 0.2296