

# Increase ferroelastic phase transition temperature of hybrid perovskite through mixed phosphonium and ammonium cation strategy

Jie Mu, Ke Xu, Lei He, Yan Xu, Ti-Jian Yin, Jin-Tao Men and Qiong Ye\*

## EXPERIMENTAL SECTION

**Syntheses.** Trimethylpropylphosphonium bromide  $[(\text{CH}_3)_3\text{PCH}_2\text{CH}_2\text{CH}_3]\text{Br}$  was synthesized as follows: First, anhydrous dichloromethane was added to the three-necked flask. After filling with nitrogen for about 15 minutes, trimethylphosphine and 1-bromopropane were then added to the flask with a syringe and the reaction solution was heated to 40 °C with stirring under reflux 3 days. Excess solvent was removed by rotary evaporation under vacuum to obtain trimethylpropylphosphonium bromide. The product was a white solid powder in about 96.5% yield. The phase purity of  $[(\text{CH}_3)_3\text{PCH}_2\text{CH}_2\text{CH}_3]^+$  was confirmed by mass spectrometry (**Fig. S1**).

**Synthesis Method of  $[(\text{CH}_3)_3\text{PCH}_2\text{CH}_2\text{CH}_3]_2(n\text{-C}_4\text{H}_9\text{NH}_3)\text{Bi}_2\text{Br}_9$  (1).** Bismuth trioxide (2 mmol, 0.9320 g), trimethylpropylphosphonium bromide (2 mmol, 0.3982 g) and *n*-butylamine (2 mmol, 0.1463 g) were successively added to hydrobromic acid solvent (50 mL) and heated and stirred until dissolved. The mixed solution was then slowly evaporated on a heating stage at 45 °C. After fifteen days, light yellow transparent bulk crystals can be obtained from the solution.

## Measurement Methods.

**Phase Purity.** Powder X-ray diffraction (PXRD) pattern was recorded with the Ultima IV X-ray diffraction instrument in the  $2\theta$  range of 5-50° with a step size of 0.02°.

**DSC Measurements.** Differential scanning calorimetry (DSC) measurements for compound **1** were carried out on the PerkinElmer Diamond DSC instrument. Powder samples of **1** (14.8 mg) were exploited in a programmed temperature control process

in the temperature range of 270 to 400 K with a heating rate of 20 K min<sup>-1</sup> under nitrogen atmosphere.

**Single-Crystal X-ray Diffraction (SCXRD).** Variable-temperature single-crystal X-ray diffraction data of compound **1** were collected using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 273 and 363 K on a Rigaku Saturn 724 diffractometer. Cell parameters were retrieved and refined using *Crystal Clear* software package on all observed reflections. The crystal structures of compound **1** were solved by direct methods and refined by the full-matrix least-squares method based on  $F^2$  by means of the *SHELXLTL* software. All non-H atoms were refined anisotropically using all reflections for which  $I > 2\sigma(I)$ . Moreover, distances and angles between atoms were calculated by *SHELXLTL*.

**Dielectric Measurements.** The complex dielectric constant ( $\epsilon = \epsilon' - i\epsilon''$ , where  $\epsilon'$  is the real part, and  $\epsilon''$  is the imaginary part) of compound **1** was tested on a Tonghui TH2828A from 300 to 400 K at 1 MHz with an AC voltage of 1 V. Moreover, the pressed-powder sample painted with silver glue was taken as the electrode.

**Ultraviolet–visible (UV–vis) absorption spectrum.** The ultraviolet-visible spectrophotometry was recorded on a Shimadzu 2600 UV-Vis spectrophotometer at room temperature in a range of 200–800 nm, using BaSO<sub>4</sub> as a standard. The optical band gap ( $E_g$ ) of **1** was estimated by converting the reflectance data to absorbance by using the Kubelka–Munk equation<sup>1</sup>:

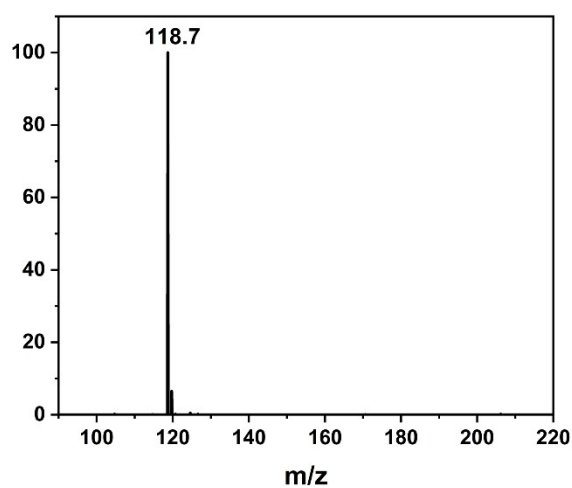
$$F(R) = (1-R)^2/2R \quad (1)$$

The  $E_g$  was calculated by using the variant of the Tauc equation<sup>2</sup>:

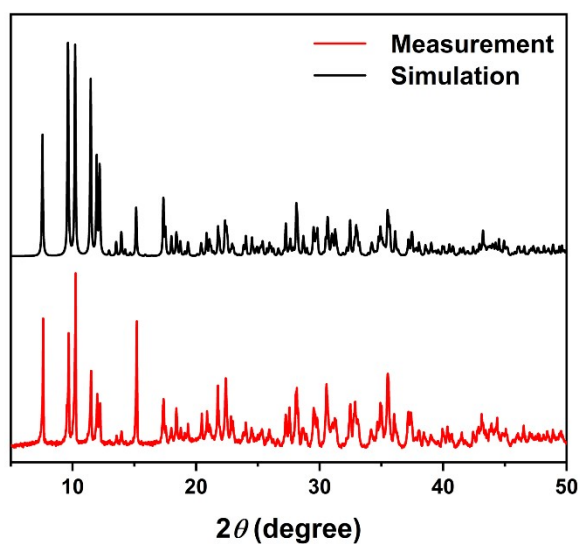
$$[h\nu \cdot F(R)]^{1/n} = A(h\nu - E_g) \quad (2),$$

$h$  = Planck's constant,  $\nu$  = frequency of vibration,  $A$  =proportional constant,  $F(R)$  is the Kubelka–Munk function, and exponent ' $n$ ' represents the nature of the sample's transition,  $n = 1/2$  for direct, and  $n = 2$  for indirect transition. The  $E_g$  can be found using a Tauc plot by plotting  $[h\nu \cdot F(R)]^{1/n}$  vs. the energy in electron volts.

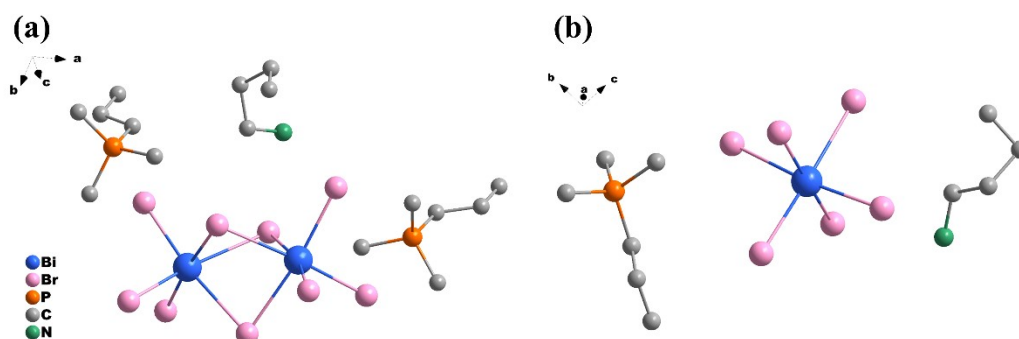
**Optical Measurements.** The single-crystal sample with a thickness of approximately 1.0 mm was placed on an Instec HCC602 cooling/heating stage. The domains were observed under an Olympus BX51TRF optical polarizing microscope. Before observing the ferroelastic domains, the crystal needs to be heated to around 360 K (high temperature phase) and then cooled to room temperature for pretreatment.



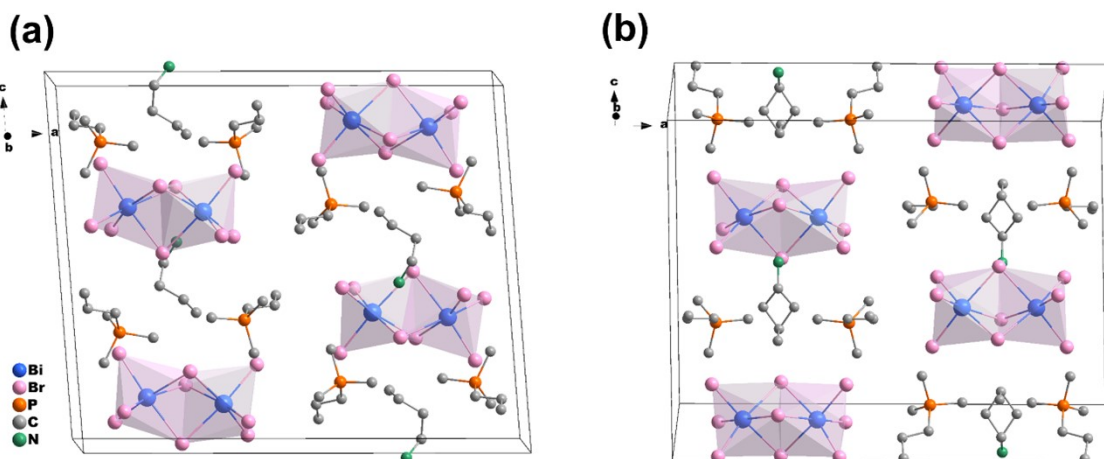
**Fig. S1** The mass spectrum of  $[(\text{CH}_3)_3\text{PCH}_2\text{CH}_2\text{CH}_3]^+$



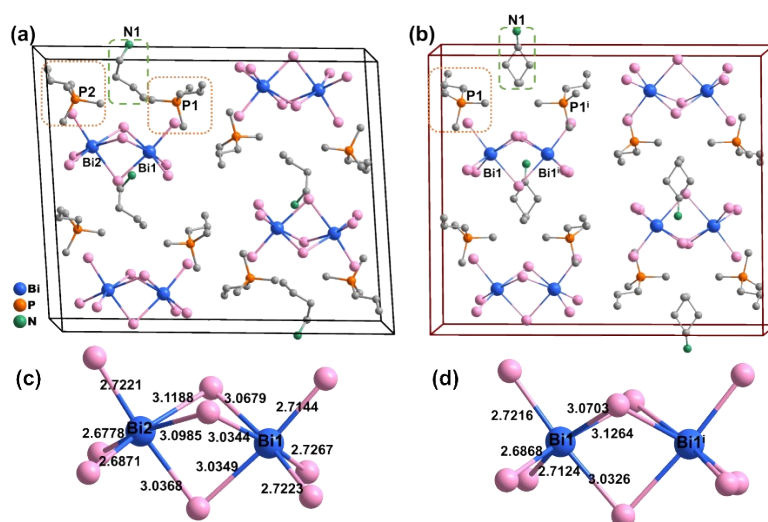
**Fig. S2** Powder X-ray diffraction patterns of compound **1** at room temperature.



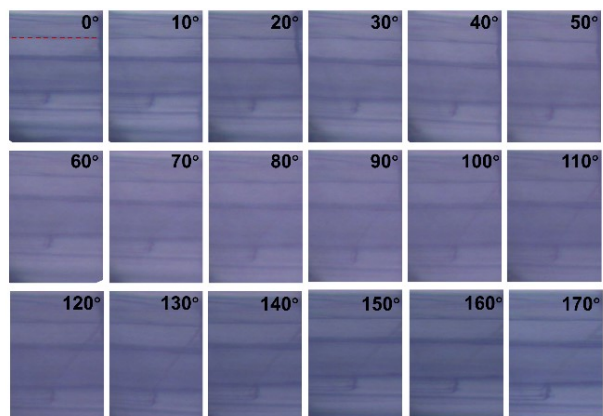
**Fig. S3** The asymmetric unit of **1** at 273 K (a) and 363 K (b).



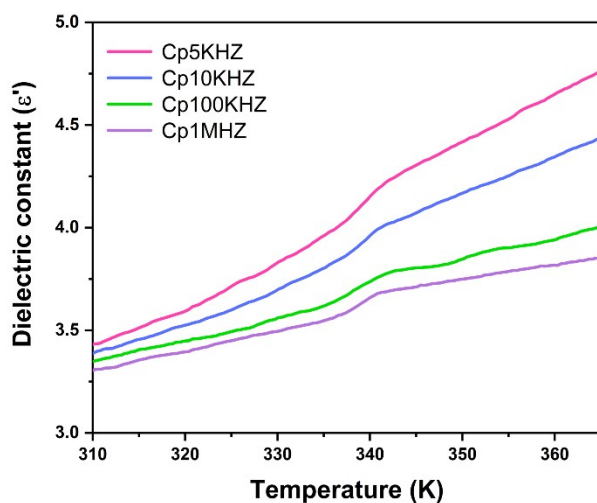
**Fig. S4** Packing structures for 1 at 273 K (a) and 363 K (b).



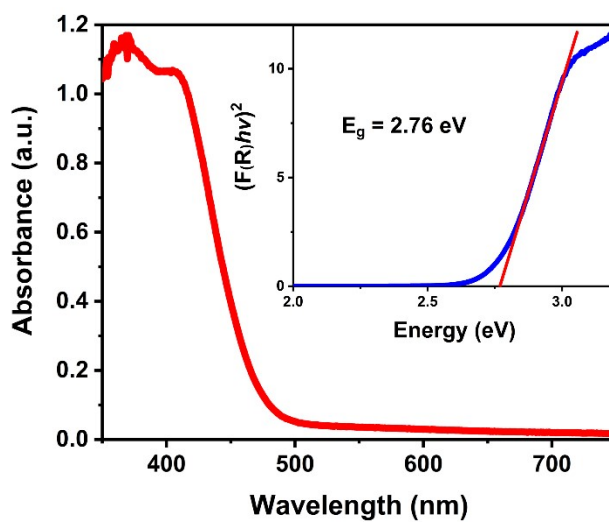
**Fig. S5** Comparison of the cell structure of 1 at 273 K (a) and 363 K (b), where the conformational changes and ordered-disordered changes of organic cations at high and low temperatures are marked with boxes. (c) shows the Bi-Br bond length of [Bi<sub>2</sub>Br<sub>9</sub>]<sup>3-</sup> anions in (a); (d) shows the Bi-Br bond length of [Bi<sub>2</sub>Br<sub>9</sub>]<sup>3-</sup> anions in (b).



**Fig. S6** Polarized light microscope images of the crystal along different angles.



**Fig. S7** Dielectric constants of **1** at 5 kHz, 10 kHz, 100 kHz, and 1000 kHz upon heating.



**Fig. S8** UV-Vis absorption spectrum of **1**.

**Table S1.** Crystal data and structure refinement details of complex **1**.

Chemical Formula	[(CH <sub>3</sub> ) <sub>3</sub> PCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ] <sub>2</sub> ( <i>n</i> -C <sub>4</sub> H <sub>9</sub> NH <sub>3</sub> )[Bi <sub>2</sub> Br <sub>9</sub> ]	
<i>T</i> (K)	273 K	363 K
Formula weight	1449.61	1449.61
Crystal system	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> <i>m c n</i>
<i>a</i> /Å	23.4595 (7)	23.522 (2)
<i>b</i> /Å	8.4198 (2)	8.5667 (6)
<i>c</i> /Å	19.3390 (6)	19.7659 (13)
$\alpha$ (deg)	90	90
$\beta$ (deg)	94.700 (3)	90
$\gamma$ (deg)	90	90
<i>V</i> /Å <sup>3</sup>	3807.08 (19)	3982.9 (5)
<i>Z</i>	4	4
<i>F</i> (000)	2632	2456
GOF	1.02	1.10
<i>R</i> <sub>1</sub>	0.095	0.110
<i>wR</i> <sub>2</sub>	0.228	0.273

**Table S2.** The bond lengths and angles at 273 K.

Bond lengths (Å)		Bond angles (°)	
Bi1—Br1	2.7144 (7)	Br1—Bi1—Br3	94.12 (2)
Bi1—Br3	2.7223 (8)	Br1—Bi1—Br2	93.44 (2)
Bi1—Br2	2.7267 (9)	Br3—Bi1—Br2	96.37 (3)
Bi1—Br6	3.0344 (7)	Br1—Bi1—Br6	92.09 (2)
Bi1—Br5	3.0349 (7)	Br3—Bi1—Br6	88.70 (2)
Bi1—Br4	3.0679 (8)	Br2—Bi1—Br6	172.21 (2)
Bi2—Br8	2.6778 (9)	Br1—Bi1—Br5	173.86 (2)
Bi2—Br9	2.6871 (8)	Br3—Bi1—Br5	89.25 (2)

Bi2—Br7	2.7221 (8)	Br2—Bi1—Br5	91.27 (2)
Bi2—Br5	3.0368 (7)	Br6—Bi1—Br5	82.853 (19)
Bi2—Br6	3.0985 (7)	Br1—Bi1—Br4	93.95 (2)
Bi2—Br4	3.1188 (7)	Br3—Bi1—Br4	167.78 (2)
P2—C9	1.769 (9)	Br2—Bi1—Br4	92.29 (2)
P2—C10	1.775 (7)	Br6—Bi1—Br4	81.851 (19)
P2—C7	1.801 (8)	Br5—Bi1—Br4	81.932 (19)
P2—C8	1.802 (7)	Br8—Bi2—Br9	96.39 (3)
P1—C3	1.756 (8)	Br8—Bi2—Br7	92.40 (3)
P1—C4	1.770 (8)	Br9—Bi2—Br7	92.14 (3)
P1—C2	1.775 (7)	Br8—Bi2—Br5	93.15 (3)
P1—C1	1.803 (8)	Br9—Bi2—Br5	88.06 (2)
		Br7—Bi2—Br5	174.39 (2)
		Br8—Bi2—Br6	172.11 (3)
		Br9—Bi2—Br6	89.48 (2)
		Br7—Bi2—Br6	92.63 (2)
		Br5—Bi2—Br6	81.764 (19)
		Br8—Bi2—Br4	93.28 (3)
		Br9—Bi2—Br4	165.83 (2)
		Br7—Bi2—Br4	97.79 (2)
		Br5—Bi2—Br4	81.072 (19)
		Br6—Bi2—Br4	80.028 (18)
		Bi1—Br6—Bi2	81.991 (17)
		Bi1—Br5—Bi2	83.004 (18)
		Bi1—Br4—Bi2	81.129 (17)
		C9—P2—C10	108.5 (4)
		C9—P2—C7	111.8 (4)
		C10—P2—C7	110.4 (4)
		C9—P2—C8	108.5 (4)
		C10—P2—C8	109.2 (3)

C7—P2—C8	108.3 (4)
C3—P1—C4	110.7 (4)
C3—P1—C2	110.1 (4)
C4—P1—C2	107.1 (4)
C3—P1—C1	110.7 (4)
C4—P1—C1	109.1 (4)
C2—P1—C1	109.0 (4)

**Table S3.** The bond lengths and angles at 363 K.

<b>Bond lengths (Å)</b>		<b>Bond angles (°)</b>	
Bi1—Br3	2.6868 (14)	Br3—Bi1—Br2	95.59 (4)
Bi1—Br2	2.7124 (14)	Br3—Bi1—Br1	93.37 (4)
Bi1—Br1	2.7216 (11)	Br2—Bi1—Br1	92.99 (4)
Bi1—Br5	3.0326 (9)	Br3—Bi1—Br5	90.28 (4)
Bi1—Br6	3.0703 (10)	Br2—Bi1—Br5	89.81 (4)
Bi1—Br4	3.1264 (10)	Br1—Bi1—Br5	175.16 (3)
Br6—Bi1 <sup>i</sup>	3.0703 (10)	Br3—Bi1—Br6	91.37 (4)
Br5—Bi1 <sup>i</sup>	3.0326 (9)	Br2—Bi1—Br6	170.77 (4)
Br4—Bi1 <sup>i</sup>	3.1263 (10)	Br1—Bi1—Br6	92.64 (3)
P1—C1	1.777 (10)	Br5—Bi1—Br6	84.09 (3)
P1—C4	1.869 (10)	Br3—Bi1—Br4	168.26 (3)
P1—C3	1.774 (11)	Br2—Bi1—Br4	91.70 (4)
P1—C2	1.788 (11)	Br1—Bi1—Br4	95.43 (3)
		Br5—Bi1—Br4	80.53 (3)
		Br6—Bi1—Br4	80.49 (3)
		Bi1 <sup>i</sup> —Br6—Bi1	81.98 (3)
		Bi1 <sup>i</sup> —Br5—Bi1	83.22 (3)
		Bi1 <sup>i</sup> —Br4—Bi1	80.21 (3)
		C3—P1—C1	109.6 (5)



---

C3—P1—C2	111.8 (5)
C1—P1—C2	104.2 (5)
C3—P1—C4	113.5 (4)
C1—P1—C4	113.7 (4)
C2—P1—C4	103.5 (4)

---

Symmetry code: (i)  $-x+3/2, y, z$ .