

Electronic Supporting Information for

The First High-Temperature Multiaxial Ferroelectric Host-Guest Inclusion Compound

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Experimental Section

Materials: All of the reagents and solvents in the synthesis were of reagent grade and used without further purification. Firstly, stoichiometric amounts of gallium chloride and 18-crown-6 were well dissolving into distilled water and methanol to get a clear solution, respectively. Then, the above solution was mixed together. Finally, stoichiometric amounts of concentrated HCl solution was dropped into the clear solution to make it acidic. The solution was filtered after stirring overnight. After slow evaporation of the clear solution at 298 K, the colorless block single crystals of **1** was synthesized, which is shown in the Supporting Information, Figure S1 with the average size of about $4 \times 5 \times 1 \text{ mm}^3$. Thermogravimetric (TG) curves reveal that the stability of **1** can be up to 446 K (Supporting Information, Figure S5).

Thin-Film Preparation: The precursor solutions of **1** were prepared by dissolving 30 mg of the as-grown crystals in 1 mL mixed solution of distilled water and methanol (molar ratio 1:1). A mixed solution (20 μL) contains 30 mg/mL **1** was dropped onto a clean indium tin oxide (ITO) coated conductive glass ITO-glass substrate ($1.5 \times 1.5 \text{ cm}$). High quality plate-shaped crystals formed on the ITO-glass substrate after the solvent slowly evaporated on a hot plate of $80 \pm 1 \text{ }^\circ\text{C}$. The thickness of the prepared films is about 1.5 μm .

Measurements: DSC, dielectric, SHG, XRD, *P-E* hysteresis loops and PFM measurements were described previously.

Table S1. The comparison of the crystal structure and physical properties toward 18-crown-6 related ferroelectrics.

| Compound | Ferroelectric phase | Intermediate phase | Paraelectric phase | Aizu notation | T_c (K) | P_s ($\mu\text{C}/\text{cm}^2$) | Ref |
|---|---------------------|----------------------------|--------------------|---------------|-----------|-------------------------------------|------------------|
| 18-crown-6 oxonium tetrachloride-gallium (III) | $Pmc2_1$ | Weak diffraction intensity | $P4_2/nmm$ | $4/mmmFmm2$ | 337, 352 | 3.9 | This work |
| catena-(m ₂ -nitrito-O,O)-bi-aqua-(18-crown-6)-barium nitrite | $Pca2_1$ | - | $Pnma$ | $mmmFmm2$ | 182 | 1.2 | 1 |
| [Hcha-(18-crown-6)] ⁺ [BF ₄] ⁻ ^a | $Pca2_1$ | - | $Cmcm$ | $mmmFmm2$ | 397 | 3.27 | 2 |
| [Hcha-(18-crown-6)] ⁺ [ClO ₄] ⁻ | $Pca2_1$ | - | $Cmcm$ | $mmmFmm2$ | 390 | 3.78 | 2 |
| 4-Methoxyanilinium Perrhenate 18-Crown-6 | $Pna2_1$ | - | $Pnma$ | $mmmFmm2$ | 153 | 1.2 | 3 |
| [(DIPA)([18]crown-6)]BF ₄ ^b | $Pna2_1$ | $Pbcn$ | $Ibam$ | $mmmFmm2$ | 305, 120 | 0.3 | 4 |
| [(DIPA)([18]crown-6)](ClO ₄) | $Pna2_1$ | $Pbcn$ | $Ibam$ | $mmmFmm2$ | 278, 132 | 0.42 | 5 |
| 4-Methoxyanilinium Tetrafluoroborate-18-crown-6 | $Pna2_1$ | - | $Pnma$ | $mmmFmm2$ | 126 | 0.54 | 6 |

^a Hcha = protonated cyclohexyl ammonium;^b DIPA = 2,6-diisopropylanilinium.**Table S2.** Crystal data and structure refinement details for compound **1**.

| Empirical formula | [(C ₁₂ H ₂₄ O ₆)(H ₃ O)]GaCl ₄ | |
|-------------------|--|--------------|
| Formula | 494.86 | |
| T (K) | 93 | 293 |
| Crystal system | orthorhombic | orthorhombic |
| Space group | $Pmc2_1$ | $Pmc2_1$ |
| $a/\text{\AA}$ | 35.430(3) | 35.489(2) |
| $b/\text{\AA}$ | 8.7631(6) | 8.9539(6) |
| $c/\text{\AA}$ | 10.0221(7) | 10.3479(9) |
| β (deg) | 90 | 90 |
| $V/\text{\AA}^3$ | 3111.6(4) | 3288.2(4) |
| Z | 6 | 6 |
| $F(000)$ | 1524.0 | 1524.0 |

| | | |
|--------------------|--------------|--------------|
| Unique reflections | 5144 | 7326 |
| Parameters refined | 335 | 334 |
| Flack parameter | 0.47(3) | 0.02(2) |
| GOF | 1.003 | 1.007 |
| R_1 | 0.0678(4252) | 0.0457(7326) |
| wR_2 | 0.1861 | 0.1047 |

Table S3. Hydrogen bond lengths (Å) and angles (°) for **1** at 293 K.

| $D-H\cdots A$ | $D-H$ (Å) | $H\cdots A$ (Å) | $D\cdots A$ (Å) | $D-H\cdots A$ (°) |
|---------------------------|-----------|-----------------|-----------------|-------------------|
| O(1)-H(1C) \cdots O(6) | 0.97 | 2.13 | 2.758(7) | 122 |
| O(1)-H(1C) \cdots O(7) | 0.97 | 1.82 | 2.693(9) | 150 |
| O(1)-H(1D) \cdots O(3) | 0.96 | 1.83 | 2.766(6) | 165 |
| O(1)-H(1E) \cdots O(5) | 0.96 | 1.80 | 2.734(9) | 167 |
| O(2)-H(2C) \cdots O(10) | 0.95 | 1.80 | 2.709(4) | 157 |
| O(2)-H(2C) \cdots O(11) | 0.95 | 2.22 | 2.776(5) | 116 |
| O(2)-H(2D) \cdots O(12) | 0.98 | 1.85 | 2.800(9) | 163 |

Table S4. According to the crystal structure data at 293 K, we select a unit cell and make an assumption that the positive charge of oxonium cation and the negative charge of tetrachloride-gallium(III) anion is on the O atom and Ga atom, respectively.

| Atoms | Coordinate | | Center coordinate |
|-------|---|---|--------------------|
| O | O1(0.1674, 0.7478, 0.7303) | O2(0.1674, 0.2522, 0.2303) | (0.5, 0.5, 0.4793) |
| | O3(0.5, 0.7532, 0.7272) | O4(0.5, 0.2468, 0.2272) | |
| | O5(0.8326, 0.7478, 0.7303) | O6(0.8326, 0.2522, 0.2303) | |
| Ga | Ga1 ¹ (0.0, 0.2692, 0.8142) | Ga1 ² (1.0, 0.2692, 0.8142) | (0.5, 0.5, 0.6178) |
| | Ga2 ¹ (0.0, 0.7308, 0.3142) | Ga2 ² (1.0, 0.7308, 0.3142) | |
| | Ga3(0.3334, 0.2309, 0.6445) | Ga4(0.6666, 0.2309, 0.6445) | |
| | Ga5 ¹ (0.3334, 0.7691, 0.1445) | Ga5 ² (0.3334, 0.7691, 1.1445) | |
| | Ga6 ¹ (0.6666, 0.7691, 0.1445) | Ga6 ² (0.6666, 0.7691, 1.1445) | |

$$P = \lim_{V \rightarrow \infty} \frac{1}{V} \sum q_i r_i$$

$$= (q_O r_O + q_{Ga} r_{Ga}) / V$$

$$\begin{aligned}
 &= [(e \times 0.4793) + (-e \times 0.6178)] \times 6 \times c / V \\
 &= [-0.1385 \times 6 \times 1.6 \times 10^{-19} \times 10.3479 \times 10^{-10} \text{ C m}] / (3288.2 \times 10^{-30} \text{ m}^3) \\
 &= -4.18 \times 10^{-2} \text{ C m}^{-2} \\
 |P_s| &= 4.18 \times 10^{-2} \text{ C m}^{-2} = 4.18 \mu\text{C cm}^{-2}
 \end{aligned}$$

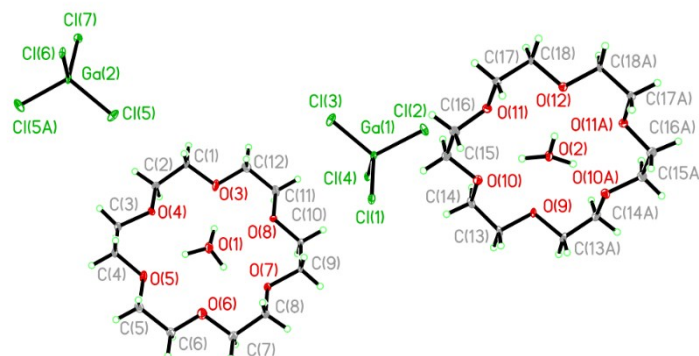


Fig. S1. Oak Ridge Thermal Ellipsoid Plot (ORTEP) at 93 K. Thermal ellipsoids are shown at the 30% probability level. The additional A letters in the atom labels indicate atoms at (1-x, y, z) for the 18-crown-6 moieties and at (2-x, y, z) for the tetrachloride-gallium(III) moieties.

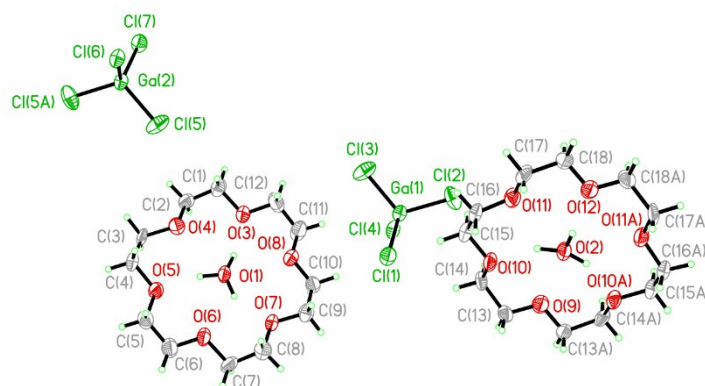


Fig. S2. ORTEP at 293 K. Thermal ellipsoids are shown at the 30% probability level. The additional A letters in the atom labels indicate atoms at (1-x, y, z) for the 18-crown-6 moieties and at (2-x, y, z) for the tetrachloride-gallium(III) moieties.

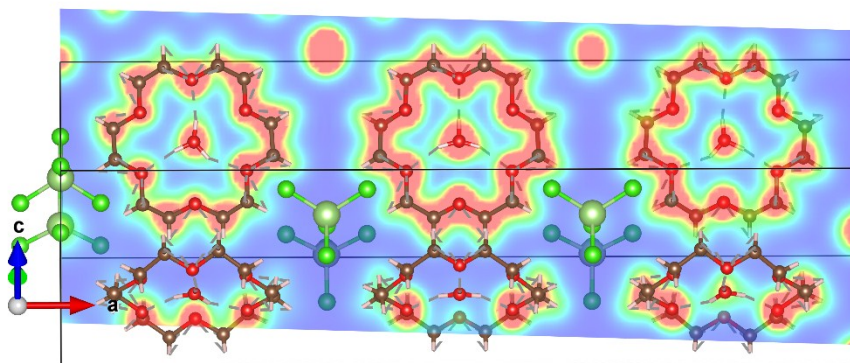


Fig. S3. Electron density distribution ((010) slice) in **1**.

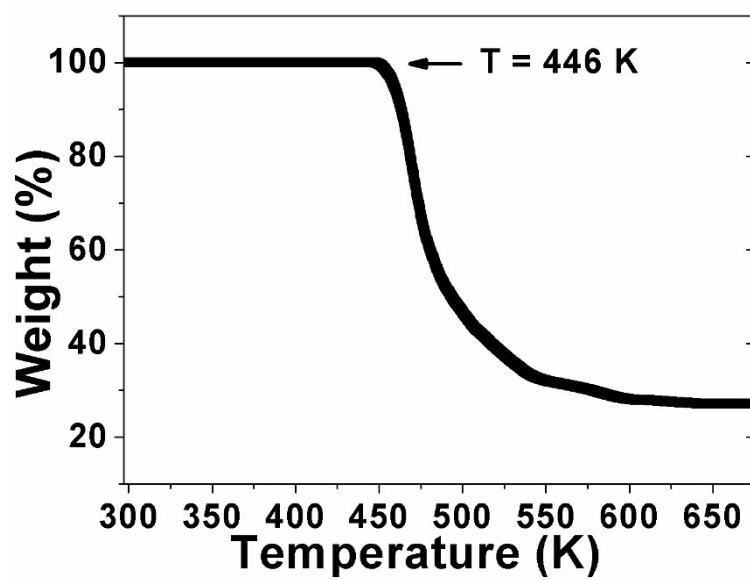


Fig. S4. The TGA result for 18-crown-6 oxonium tetrachloride-gallium(III) (**1**).



Fig. S5. The morphology of **1**.

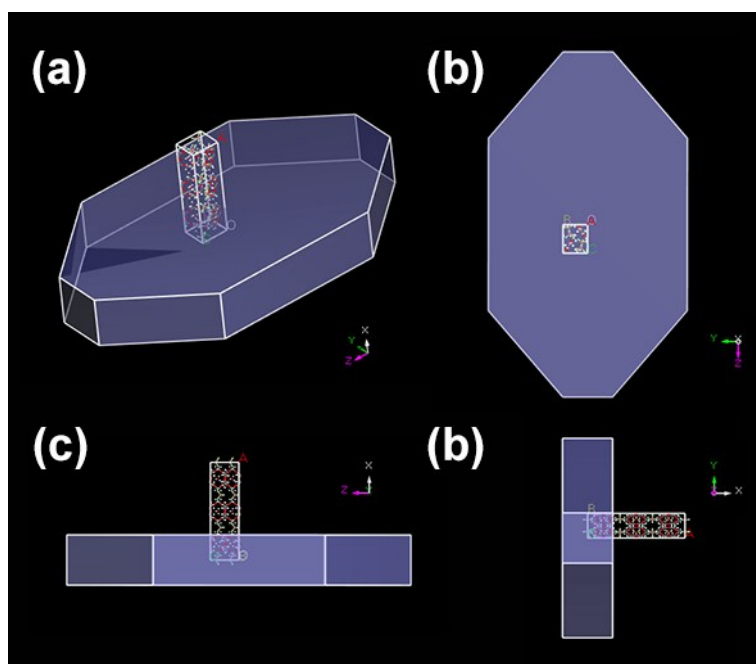


Fig. S6. The simulated morphology of the crystal **1** from a random perspective (a) and the crystallographic (b) *a*, (c) *b* and (d) *c*-axes. The crystallographic *a*, *b* and *c*-axes is corresponding to the *x*, *y* and *z*-axes marked in the crystal.

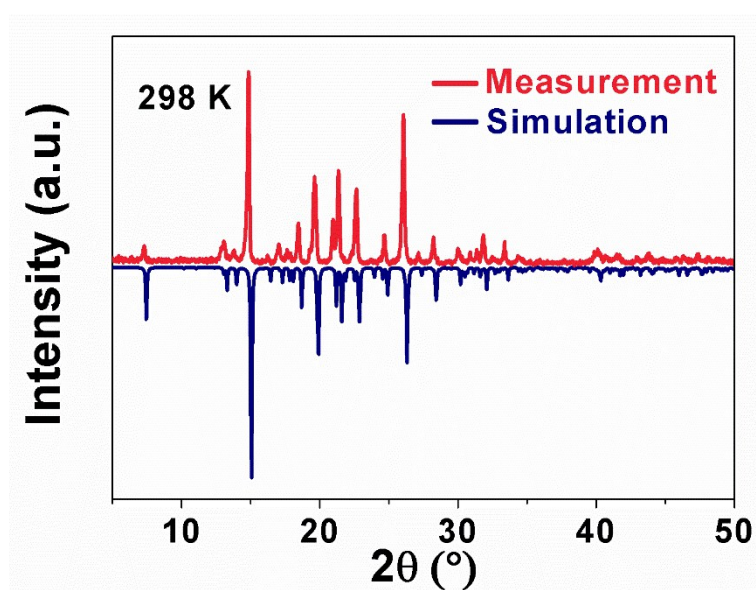


Fig. S7. The PXRD pattern of **1** measured at 298 K matches well with the simulated one based on the single crystal structure, indicating the purity of the phase.

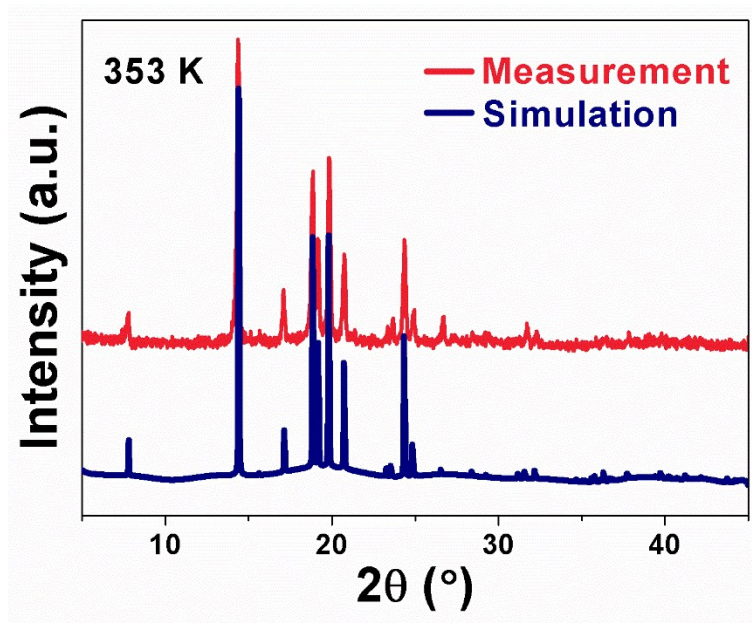


Fig. S8. The measured and simulated X-ray diffraction pattern of 1 at 353 K.

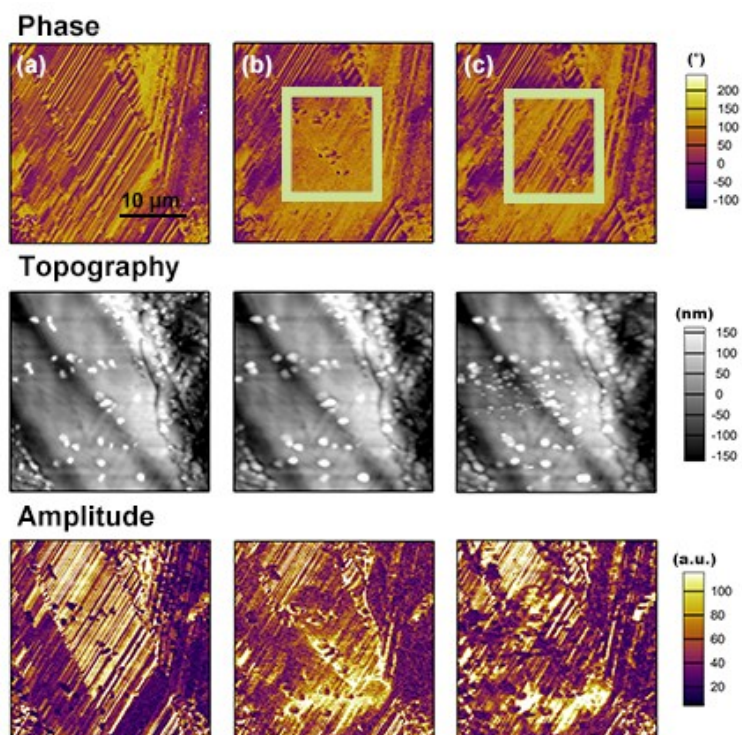


Fig. S9. Panels in each column are arranged as the following sequence: phase (above), topography (middle), and lateral PFM amplitude (below) images of the thin-film surface. (a) Initial state. (b) After the first switching produced by scanning with the tip bias of +70 V. (c) After the succeeding back-switching produced by scanning with the tip bias of -70 V.

Reference:

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