Oral presentation

Resolving the origins of ferroelectricity in hexagonal barium titanate

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Ferroelectrics form critical components of contemporary electronic devices owing to their appealing electromechanical properties. The cubic perovskite $BaTiO_3$ comprises one of the most renowned ferroelectric materials, where ferroelectricity occurs due to an off-centre displacement of the octahedral Ti^{4+} cations along the <111> directions [1]. While the cubic polytype of $BaTiO_3$ (3C-$BaTiO_3$) has been closely scrutinised for its ferroelectric properties, its six-layer hexagonal (6H) counterpart (**Fig. 1a**) has received far less scrutiny. As a polymorph of the more familiar cubic perovskite structure, 6H-$BaTiO_3$ serves as an excellent prototype system to explore how local <111>-type Ti^{4+} displacements transfer to more complex structural topologies [2] and reveal how appealing ferroic properties may be generated in materials featuring a greater diversity of cation geometries. 6H-$BaTiO_3$ exhibits two dielectric anomalies at 222 K (T_o) and 74 K (T_c); ferroelectric hysteresis has been observed below T_c [3], confirming 6H-$BaTiO_3$ adopts a ferroelectric ground state. However, the mechanism of ferroelectricity remains contentious to this day [4,5] owing to insufficient structural characterisation, so it is unclear what drives the emergence of the low-temperature ferroelectric state in this material.

Here, we revisit the anomalous mechanism of ferroelectricity in 6H-$BaTiO_3$ by re-examining its prior structural characterisation. Our structural investigations and subsequent symmetry analysis evoke a scenario in which a gradual rotation of the primary piezoelectric order parameter at T_c unlocks the capacity for an improper ferroelectric component to emerge. Atomistically, the ferroelectric distortion resembles the pattern of Ti^{4+} displacements observed in the 3C polytype, showing that the picture of local <111>-type Ti^{4+} displacements is transferable to the rich phase space offered by polytypic perovskite materials. Local structural fluctuations associated with the domain walls suggest that these displacements are preserved above the canonical ferroelectric transition temperature so that the domain walls possess the capacity for ferroelectricity even within the temperature regime of the intermediary structural state ($T_c < T < T_o$). Ferroelectricity in 6H-$BaTiO_3$ thus emerges from a highly complex domain structure (**Fig. 1b**) similar to that found in other improper ferroelectrics such as $R$$MnO_3$ (R = Sc, Y, Dy–Lu) [6], though ferroelectricity in 6H-$BaTiO_3$ is driven by coupling to a piezoelectric mode (rather than a polyhedral tilting distortion). 6H-$BaTiO_3$ represents an intriguing system in which to study how the interplay between piezoelectric, ferroelectric, and ferroelastic distortions can yield rich domain textures with appealing functional implications.

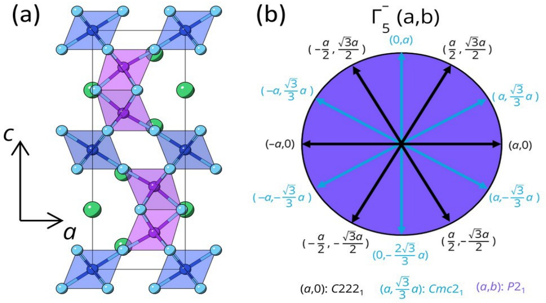

Figure 1. (a) Aristotypical structure of 6H-$BaTiO_3$ (space group: $P6_3/mmc$). Corner-sharing and face-sharing TiO_6 octahedra are shown in blue and purple, respectively. (b) Domain structure of 6H-$BaTiO_3$ depicted with respect to the order parameter space of the piezoelectric order parameter, which transforms with respect to the high-symmetry aristotype structure as the Γ^{-} irrep.

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