

Observation of ferroelectric polarization in hybrid improper ferroelectric $(\text{Ca, Sr})_3\text{Ti}_2\text{O}_7$

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Hybrid improper ferroelectric $(\text{Ca, Sr})_3\text{Ti}_2\text{O}_7$ has attracted much attention because of the peculiar mechanism to induce ferroelectricity, i.e., the electric polarization is achieved by a combination of two non-polar rotations of oxygen octahedral. In addition, it is reported that $(\text{Ca, Sr})_3\text{Ti}_2\text{O}_7$ shows abundant head-to-head and tail-to-tail charged domain walls [1], although such ferroelectric domain walls are unfavorable in terms of the electrostatic energy. Several mechanisms to stabilize the head-to-head and tail-to-tail charged domain walls have been proposed [2, 3]. Recent observations using high-angle annular dark-field scanning transmission microscopy suggested that the electric polarization exists within the charged domain walls to reduce the electrostatic energy [3]. However, the ferroelectric behavior (electric polarization) at charged domain walls has not been observed directly.

Here we investigated the microstructure and electric polarization of head-to-head (tail-to-tail) charged domain walls in $\text{Ca}_{2.46}\text{Sr}_{0.54}\text{Ti}_2\text{O}_7$ (CSTO) using transmission electron microscopy. We further performed electron holography to directly determine the direction of electric polarization and to observe electric fields in the vicinity of the charged domain walls. Single crystals of CSTO were grown by the floating zone method. Thin specimens for TEM studies were prepared by using a focused ion beam system. The observations were carried out using transmission electron microscopes (JEM-2100, JEOL Ltd. and HF3300X, Hitachi Ltd.). A dark-field TEM observation revealed irregular-shaped, four types of antiphase domain walls which are attributed to two octahedral (TiO_6) rotations (Figure 1), referred to as Z_4 vortex [4]. Systematic dark-field image observations determined the directions of electric polarizations that were tilted off from the antiphase domain walls by approximately 45° . We will discuss the anomaly in electric potential in those charged domain walls based on the electron holography observations. The results provide further insights for understanding of the nature of the charged domain walls.

This study was supported by JST, CREST (JPMJCR1664). [1] Y. Oh et al., *Nat. Mater.* **14**, 407 (2015). [2] F. Hung et al., *Nat Comm.* **7**, 11602 (2016). [3] M. Lee et al., *PRL* **119**, 157601 (2017). [4] F. Huang and S.-W. Cheong *Nat. Rev. Mater.* **2**, 17004 (2017).

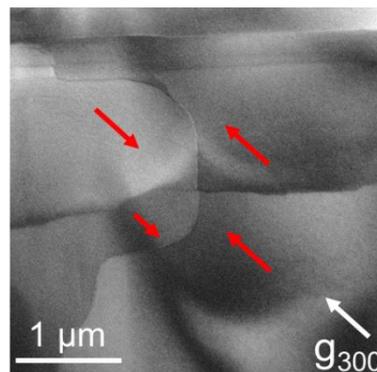


Figure 1. Dark-field image using a superlattice spot 003 in $\text{Ca}_{2.46}\text{Sr}_{0.54}\text{Ti}_2\text{O}_7$. The red arrows show the direction of the electric polarization.