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Direct Observation of ferroelectric domain walls in improper ferroelectric $(Ca,Sr)_3Ti_2O_7$

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Recently a large number of functional materials such as ferroelectric materials [1-3] and half-Heusler semiconductors with large polarization [4] have been proposed based on theoretical first-principles calculations, some of which have been confirmed experimentally. For example, new hybrid improper ferroelectric compounds such as $Ca_3Ti_2O_7$, $Ca_3Mn_2O_7$ and $(Ca/Sr/Ba)_3(Sn/Zr/Ge)_2O_7$ with the Ruddlesden-Popper structure (Fig. 1(a)) were suggested to show ferroelectricity from recent first-principles calculations [5]. In these compounds, it is anticipated that the structural phase transition from a paraelectric $I4/mmm$ structure to the ferroelectric $A2_1am$ structure is driven by two distinct octahedral rotations with different symmetries and the net ferroelectric polarization along the [100] direction should originate from antipolar displacements of Ca/Sr/Ba ions in the Rocksalt layer of the Ruddlesden-Popper structure. Note that hybrid improper ferroelectric compounds are characterized as the improper ferroelectric compounds, in which the order parameter of the phase transition is not the polarization but another physical quantity such as non-polar octahedral rotations [6]. The spontaneous polarization arises in the phase transition as a secondary effect [6]. The coupling between the spontaneous ferroelectric polarization and other physical quantities should result in unique domain structures in some improper ferroelectric materials such as gadolinium molybdate [7]. Recently Oh *et al*. succeeded in preparing single crystals of hybrid improper ferroelectric $(Ca,Sr)_3Ti_2O_7$ and found the intriguing ferroelectric domain structure consisting of abundant charged domain walls with conducting head-to-head and insulating tail-to-tail configurations [8]. In this work, using state-of-the-art aberration-corrected bright-field (BF) and high-angle annular-dark-field (HAADF) scanning transmission electron microscopy (STEM), we investigated ferroelectric domain wall structures in improper ferroelectric $(Ca,Sr)_3Ti_2O_7$ at the atomic scale. We succeeded in observing directly three distinct types of ferroelectric domain walls, i.e., non-charged 180° domain walls, head-to-head type charged domain walls and tail-to-tail type charged domain walls, in the ferroelectric phase.

Single crystals of $(Ca_{1-x}Sr_x)_3Ti_2O_7$ for x=0.54 were prepared by optical floating zone method. Cross sectional thin samples for transmission electron microscopy (TEM) were prepared by focused ion beam (FIB) techniques. BF and HAADF-STEM observations were performed using a JEM-ARM 200F, providing a 0.1 nm electron beam diameter and a 24-27mrad convergence semi-angle. The inner and outer collection semi-angles of the annular dark-field detector were 90 and 370 mrad, respectively.
Figure 1(b) shows a dark-field TEM image obtained at 298 K in single crystal of $(Ca_{1-x}Sr_x)_3Ti_2O_7$ for x=0.54. As shown in Fig. 1(b), dark field image, which was obtained under the two beam condition of g=202, revealed the presence of charged domain walls with head-to-head and tail-to-tail configurations, in addition to the non-charged 180° ferroelectric domain walls. Note that the arrows in Fig. 1(b) indicated the direction of spontaneous polarization vectors. Alternative regions with bright and dark contrasts should correspond to the ferroelectric domains. Thus, in order to clarify ferroelectric domain wall structures at the atomic scale, we investigated high-resolution BF- and HAADF-STEM images of non-charged 180° ferroelectric domain walls and charged domain walls with head-to-head and tail-to-

tail configurations. The [010] projection is particularly useful for imaging the ferroelectric domain walls because spontaneous polarization is easily determined by examining displacements of local Ca/Sr ions. Figure 1(c) is a [010] projected HAADF-STEM image obtained from the area indicated by the solid circle in Fig. 1(b), which shows the presence of the non-charged 180° ferroelectric domain wall. In Fig. 1(c), bright dots can be identified as the Ca/Sr columns and displacements of the Ca/Sr ions along the [100] direction can be easily resolved. Note that rows consisting of five bright dots along the [001] direction should correspond to the Ca/Sr and Ti ions, as shown in Fig. 1(c). We also investigated ferroelectric domain wall structures with head-to-head and tail-to-tail configurations and observed directly them by obtaining some HAADF-STEM images. It was revealed that displacement patterns of the Ca/Sr ions in the domain wall structures are eventually different from those of the domain structures [9].

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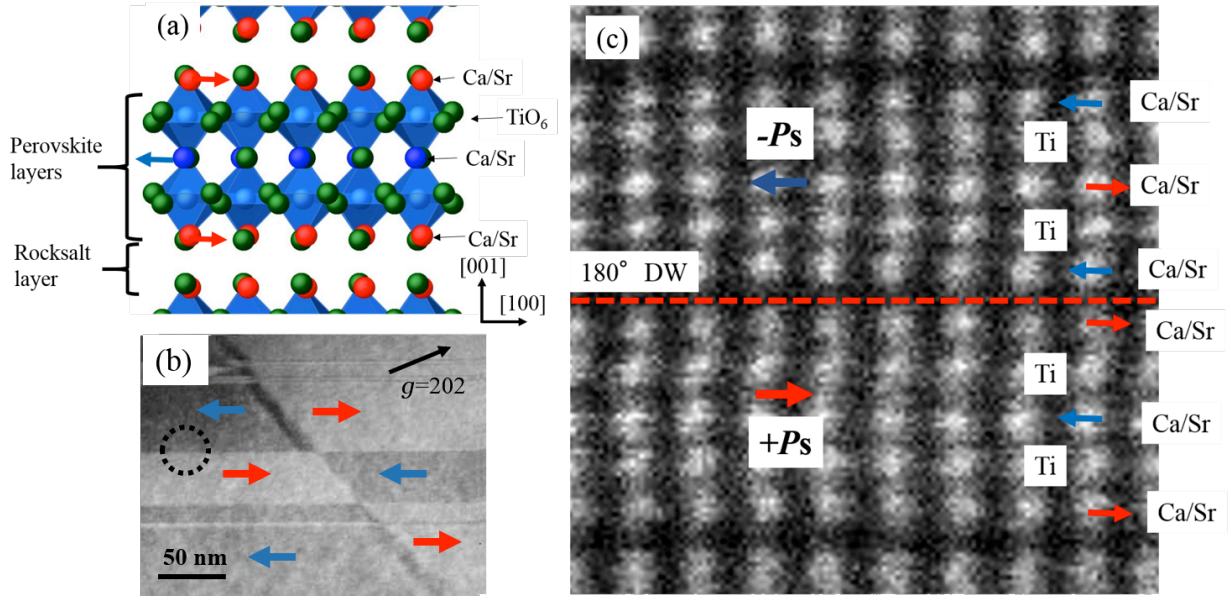

Figure 1. (a) Crystal structure of $(Ca_{1-x}Sr_x)_3Ti_2O_7$ with the Ruddlesden-Popper structure. (b) dark-field image exhibiting ferroelectric domain structure with non-charged 180° domain walls and charged (head-to-head and tail-to-tail) domain walls in $(Ca_{1-x}Sr_x)_3 Ti_2O_7$ for x=0.54. (c) A typical HAADF-STEM image showing the non-charged 180 ° ferroelectric domain wall.

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