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IT-9-O-2923 Study of nanoscale local structures of ferroelectric barium titanate using convergent-beam electron diffraction

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Convergent-beam electron diffraction (CBED) is established as the most powerful technique to determine crystal point- and space-groups from nanometer-sized specimen areas.[1)] The CBED method was extended to quantitative crystal structure analysis by Tsuda and Tanaka,[2, 3)] which enables determinations of structural parameters such as atom positions, atomic displacement parameters (ADPs), as well as electrostatic potential and electron density distributions. In the present study, we applied the CBED method to examine nanometer-scale local structures of $BaTiO_3$.

It is well known that $BaTiO_3$ undergoes successive phase transformations from the cubic paraelectric phase to three ferroelectric phases: tetragonal, orthorhombic and rhombohedral ones. Coexistence of the displacive and order-disorder characters in the phase transformations of BaTiO3 was pointed out from many experiments and theories. However, local structures related to the order-disorder character were discovered neither in crystal structure analyses using neutron and X-ray diffraction nor by TEM observations.

Using the CBED method, rhombohedral nanostructures were observed in the orthorhombic and tetragonal phases of $BaTiO_3$.[4)] It was found that the symmetry of the orthorhombic phase is formed as the average of two rhombohedral variants with different polarizations, and that of the tetragonal phase is formed as the average of four rhombohedral variants. These results indicate an order-disorder character in their phase transformations.4) Similar results were obtained in the ferroelectric orthorhombic phase of $KNbO_3$,[5)] while it was found that the ferroelectric tetragonal phase of $PbTiO_3$ does not have such rhombohedral nanostructures.[6)]

We also proposed a combined use of STEM and CBED methods (STEM-CBED method[7)]) to observe the nanostructures of polarizations, which is schematically shown in Fig. 1. Using the STEM-CBED method, two-dimensional distributions of the rhombohedral nanostructures, or nanoscale fluctuations of the polarization clusters, were successfully visualized in the tetragonal phase of $BaTiO_3$ as shown in Fig. 2.

References

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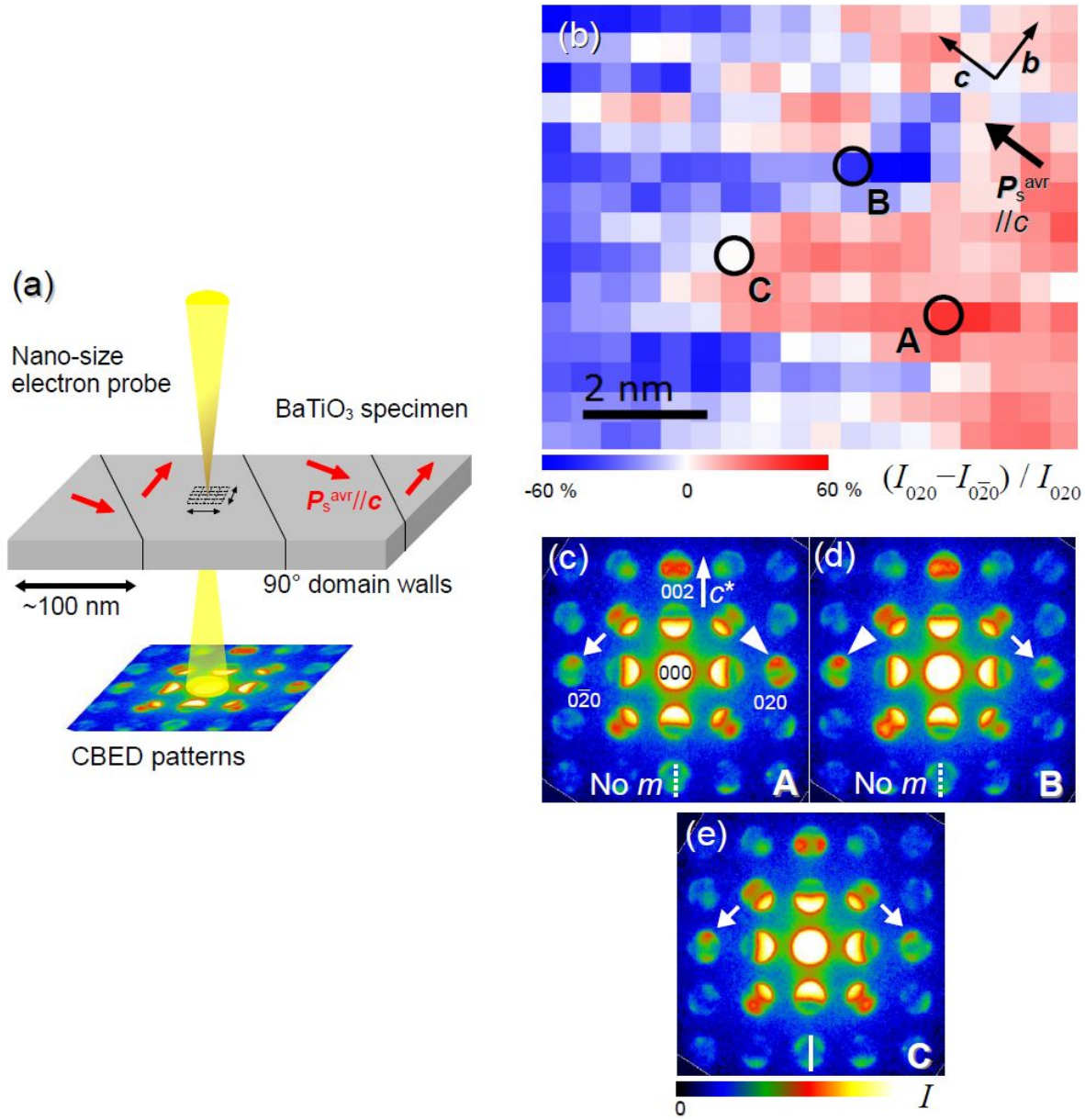

Fig. 1: (a) Schematic diagram of the STEM-CBED method.[7] (b) a STEM-CBED map of the tetragonal $BaTiO_3$ and CBED patterns,[7] which shows the intensity difference between the 020 and 0-20 reflections, $(I_{020}-I_{0\text{-}20})/I_{020}$. The CBED patterns obtained at positions A, B, and C are, respectively, shown in (c), (d), and (e).