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Study of nanoscale local structures of ferroelectric barium titanate using CBED

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It is well known that BaTiO3 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. In the present study, the convergent-beam electron diffraction (CBED) method was applied to examine nanometer-scale local structures of BaTiO3. Rhombohedral nanostructures were observed in the orthorhombic and tetragonal phases of BaTiO3 using CBED [1]. 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. Similar results were obtained in the ferroelectric orthorhombic phase of KNbO3 [2], while it was found that the ferroelectric tetragonal phase of PbTiO3 does not have such rhombohedral nanostructures. We also proposed a combined use of STEM and CBED methods (STEM-CBED method) to observe the nanostructures of polarizations [3]. Using the method, two-dimensional distribution of the rhombohedral nanostructures, or nanoscale fluctuations of the polarization clusters, were successfully visualized in the tetragonal phase of BaTiO3.

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