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Mapping Of Nanoscale Structural Fluctuations In Ferroelectric $BaTiO_3$ Using STEM-CBED

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The convergent-beam electron diffraction (CBED) method has become established as the most powerful technique for determining crystal symmetries of specimen areas of a few nanometers in diameter [e.g. 1]. The CBED method was extended to quantitative crystal structure analysis for determining structural parameters such as atom positions, atomic displacement parameters (ADPs) and electrostatic potential distributions [2-4]. To examine nanometer-scale variations of local structures, we proposed a combined use of scanning the transmission electron microscopy (STEM) and the CBED (STEM-CBED method). The STEM-CBED method enables us to visualize nanometer-scale spatial distributions of local structures with picometer-scale sensitivity to atom-displacements because of a full use of the two-dimensional angular distributions of diffraction intensities [5].

The STEM-CBED experiments are conducted using a JEM-2010FEF transmission electron microscope equipped with an Omega-type energy filter and a STEM unit with a Gatan STEM diffraction imaging system. The energy filtering is very effective for reducing inelastically-scattered background intensities in CBED patterns. Energy-filtered CBED patterns are acquired pixel-by-pixel by scanning the convergent-beam electron probe with a sub-nanometer scan step [5]. A similar technique called scanning CBED was developed by Kim *et al.* [6].

We have applied the STEM-CBED method to perovskite-type ferroelectric oxides like $BaTiO_3$. Despite extensive studies over many decades, the mechanism of their structural phase transformations has been a matter of discussion [e.g. 7, 8]. Examinations of their nanometer-scale local structures are crucial to resolve this problem. In the tetragonal phase of $BaTiO_3$, two-dimensional distributions of nanoscale fluctuations of the rhombohedral polarization clusters were visualized from the STEM-CBED patterns [5]. It was revealed that the tetragonal phase of $BaTiO_3$ is formed as the average structure of the variants of the rhombohedral nanostructures with different orientations of polarizations. Similar rhombohedral nanostructures were observed in the orthorhombic phase of $KNbO_3$ [9]. These show the order-disorder character in the phase transformations. The scales of spatial correlations of the local polarizations can be related to the transition entropy [9].

It is also very important to investigate the local structures of the paraelectric cubic phase of $BaTiO_3$ above the Curie temperature of T_c=403 K because precursors of the phase transformation are expected to exist in the cubic phase. Figures 1(a) and 1(b) show energy-filtered CBED patterns of the cubic phase of $BaTiO_3$ taken at 415 K and 460 K, respectively. It is seen that the pattern taken at 415 K exhibits clear breaking of the fourfold rotation symmetry expected from the cubic phase, while the pattern taken at 460 K shows almost the fourfold rotation symmetry. This indicates that there exist local polarization clusters in the cubic phase, and the polarization clusters are decreased with increasing temperature. A symmetry-breaking index of the CBED pattern was mapped from the STEM-CBED patterns. The details will be presented in the talk. [10]

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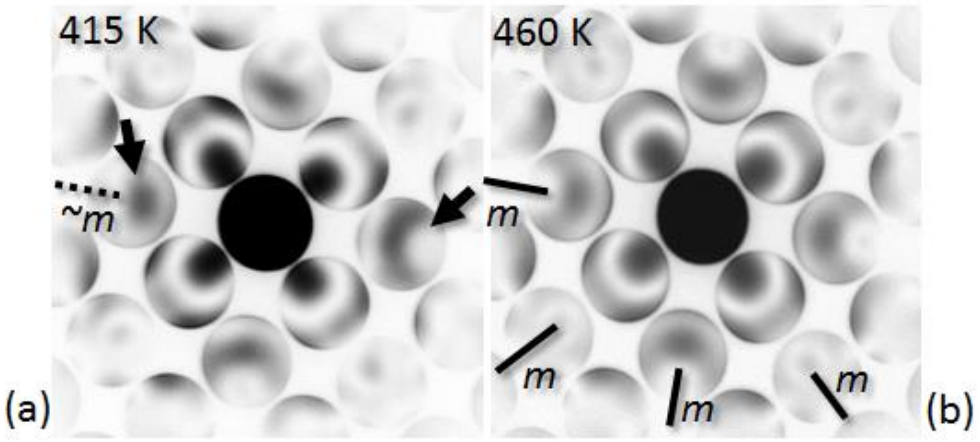

Figure 1. Energy-filtered [100] CBED patterns of the cubic phase of $BaTiO_3$ taken at specimen temperatures of (a) 415 K and (b) 460 K. The pattern (a) exhibit clear breaking of the fourfold rotation symmetry expected from the cubic phase, while the pattern (b) shows almost the fourfold rotation symmetry.