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Local Crystal Structure Determination based on Annular Dark-Field Imaging and its application for Perovskite Manganites

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In the study for recent advanced materials, the investigation of local microstructure is indispensable. Here we demonstrate a crystal structure refinement based on the annular dark field (ADF)[1] imaging of the scanning transmission electron microscopy (STEM). Although conventional high-resolution transmission electron microscopy (HRTEM) has been effective for analyzing a microstructure, the crystal structure and the chemical composition cannot be easily interpreted based on the coherent bright field images. On the other hand, it is well known that a STEM-ADF imaging[1] provides an incoherent image, in which bright spots correspond to atomic positions and the intensity of the bright spots is sensitive to its atomic number. In spite of its superior imaging properties, technological barrier, *e.g.*, quantum noise or image distortion caused by long time exposition involving with weak high-angular scattering, prevents from performing a quantitative analysis for a STEM-ADF image.

We developed the mechanically and electrically stabilized STEM instrument (Hitachi High Technologies HD-2300C)[2] and customized software which performs a high speed multiple image scanning and image integration with compensating the specimen drifts occurred during scanning. We obtained a high accuracy ADF image with a high signal-to-noise (S/N) ratio and with a minimum distortion. In this work, the local microstructures of the *A*-site ordered/disordered perovskite manganite[3], $Tb_{0.5}Ba_{0.5}MnO_3$, were observed by ADF imaging with high speed multiple scanning (FIG. 1(b)) and then the 50 scanned images were integrated (FIG. 1(a)) with compensating specimen drifts. Furthermore, image simulations (FIG. 1(c)) based on multislice algorithm[4] were performed to analyze the high accuracy ADF image. FIG. 2 shows the intensity profiles on the experimental/simulated ADF images of the ordered $Tb_{0.5}Ba_{0.5}MnO_3$ crystal. Two kinds of intensity peaks on the experimental ADF image can be seen at *A*-site positions and the periodicity between the same kind of peaks corresponds to twice that of the primitive perovskite unit cell. The difference and the periodicity are well fitted with the simulated ADF image based on the crystal structure model obtained by the neutron diffraction[5]. Therefore, the *A*-site order, that Tb(001) and Ba(001) layers are alternatively stacked, can be detected by the experimental ADF image. FIG. 2 also shows displacement of intensity peak position corresponding to Mn atom from the intermidiate position between Tb and Ba layers. Statistical analysis of Mn positions revealed that Mn layers are displaced from the primitive position of a perovskite structure. It seems that the displacement is attributed to change of the optimum position of Mn atom caused by the different ionic radius of the ordered Tb and Ba atoms.

In summary, a high accuracy ADF imaging can be widely applied for recent advanced materials, such as CMR[3] materials or ferroelectric materials, which involve a small displacement of a cation with 10 pm order.

References

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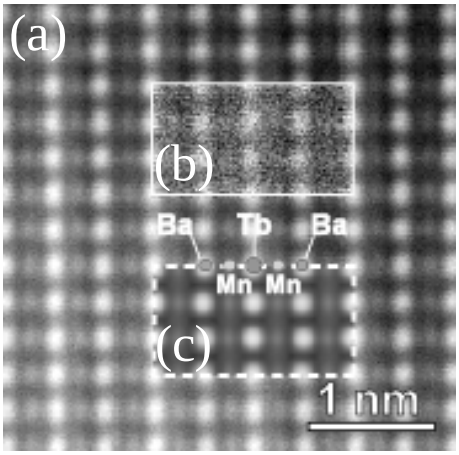

FIG. 1. (a) Integrated ADF image of the A-site-ordered $Tb_{0.5}Ba_{0.5}MnO_3$ crystal (integrated with 50 high-speed-scanning images). (b) Single high-speed-scanning image. (c) Simulated image.

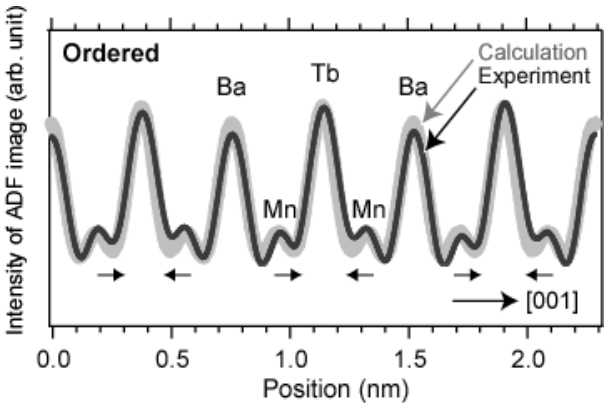

FIG. 2. Intensity profiles measured on the simulated/experimental ADF images for the A-site-ordered $Tb_{0.5}Ba_{0.5}MnO_3$ crystal.

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