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Crystal Structure Analysis Using Annular Dark-Field Imaging with High Precision

K. Kimoto*, K. Ishizuka**, M. Saito***, T. Nagai*, X. Yu*, R.-J. Xie*, N. Hirosaki*, and Y. Matsui*

* National Institute for Materials Science, Tsukuba, Ibaraki, 305-0044, Japan
** HREM Research Inc., Higashimatsuyama, Saitama, 355-0055, Japan.
*** WPI Advanced Institute for Materials Research, Tohoku University, Sendai, 980-8577, Japan

Annular dark-field (ADF) imaging in scanning transmission electron microscopy (STEM) is effective for analyzing a local crystal structure with high spatial resolution [1,2]. Recently, it has been applied for various materials, because of their compositional sensitivity and intuitive interpretability. ADF imaging, however, has a few disadvantages. One is a shot noise, *i.e.,* a low signal-to-noise (SN) ratio, because it utilizes low-intensity high-angle scattering. The other disadvantage of ADF imaging is image distortions owing to specimen drifts. Due to these disadvantages, ADF imaging is often qualitative, despite its superior imaging properties. We have applied ADF imaging for a local crystal structure analysis with high precision. The above-mentioned disadvantages of ADF imaging are solved using a stabilized STEM instrument (Hitachi High-Technologies, HD-2300C) and customized software based on DigitalMicrograph (Gatan) scripts. A spherical aberration corrector is not attached to our STEM instrument, however a high-spatial resolution of about 0.1 nm is realized [3,4]. The SN ratio of the STEM images is substantially improved by acquiring many STEM images with short dwell time using the script prepared by the authors. Maximum-entropy deconvolution (HREM Research Inc., DeConvHAADF) is utilized to enhance the spatial resolution. Here we show two examples; (i) observation of a single Eu dopant in beta-SiAlON[5], and (ii) detection of 10-pm atomic displacement in $(Tb_{0.5},Ba_{0.5})MnO_3$ [6].

Figure 1 shows the crystal structure of Eu-doped beta-SiAlON, which has beta-Si_3N_4 crystal structure. We observe bright-field (BF) and ADF images with high SN ratio (Fig. 2). An Eu-dopant contrast is observed on an atomic channel along the *c* axis. The TEM specimen thickness is evaluated as 8 nm based on the comparison between experimental BF image and multislice simulations (HREM Research Inc., xHREM). Then we quantitatively compared the dopant contrast with the simulation results (Fig. 3). We conclude that the observed contrast is a single Eu atom.

Figure 4 shows two crystal structures; *A*-site disordered and ordered $(Tb_{0.5},Ba_{0.5})MnO_3$, respectively. The both crystal structures are basically perovskite manganite $AMnO_3$. Neutron diffraction analysis shows that Mn sites of *A*-site ordered specimen (Fig. 4b) are shifted to Tb atomic site by 8 pm owing to the difference of ionic radii between Tb and Ba. We observed BF (not shown) and ADF images of the two specimens (Fig. 5). The distances between *A*-site and Mn site are measured and their histogram is shown in Fig. 6. It is clear that the Mn atomic site is shifted by about 10 pm.

The quantitative STEM analysis does not always require a sub-Angstrom probe. In our study, experimental techniques to realize high SN ratio and simultaneous acquisition of BF and ADF images are effective to achieve a quantitative analysis.

[1] S. J. Pennycook, L. A. Boatner, *Nature* 336 (1988) 565.

[2] N. Shibata, S. J. Pennycook et al., *Nature* 428 (2004) 730.
[3] K. Kimoto, K. Nakamura et al., *J. Electron Microsc.* 56 (2007) 17.
[4] K. Kimoto, T. Asaka et al., *Nature* 450 (2007) 702.
[5] K. Kimoto, R.-J. Xie et al., *Appl. Phys. Lett.* 94 (2009) 041908.
[6] M. Saito, K. Kimoto et al., *J. Electron Microsc.* in print (2009)
[7] We thank Prof. Ikuhara, Dr. Shibata, Dr. Mizoguchi, and Dr. Suenaga for invaluable discussions and Drs. Wilbrink and Nakamura for the STEM development. The manganite specimens were provided by Prof. Kuwahara and Dr. Akahoshi. This work is partly supported by JST-CREST and Nano-net by MEXT.

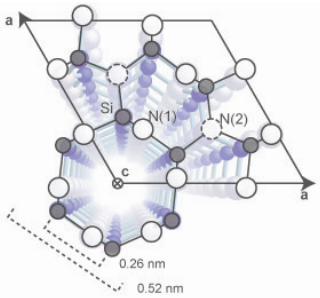

Fig. 1. Beta-Si_3N_4 crystal structure projected along [001]. Dopant Eu atoms are considered to be on the origin.

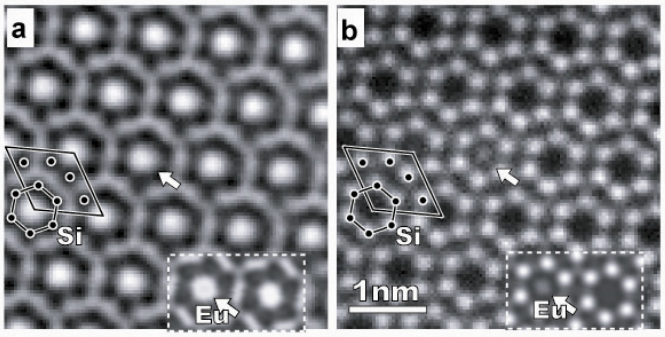

Fig. 2. (a) BF and (b) ADF STEM images of Eu-doped beta-SiAlON observed by our technique. Insets in dotted rectangles show simulation results. White arrows show Eu atom positions.

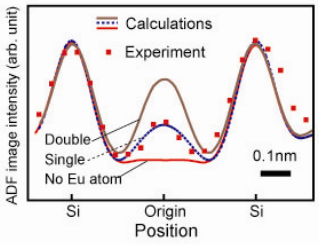

Fig. 3. Line profiles of ADF image across atomic channel. Solid and dotted lines indicate calculation results obtained by varying the number of Eu atoms

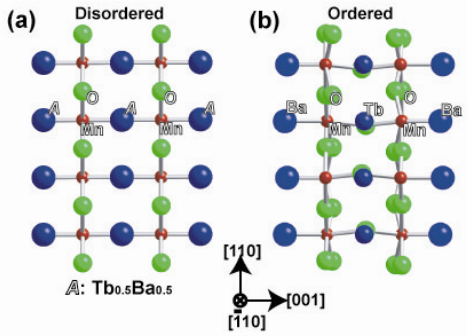

Fig. 4. Crystal structures of $Tb_{0.5}Ba_{0.5}MnO_3$ projected along the [-1 1 0] axis. (a) Disordered phase with cubic perovskite structure. (b) Ordered phase with triclinic distorted perovskite structure.

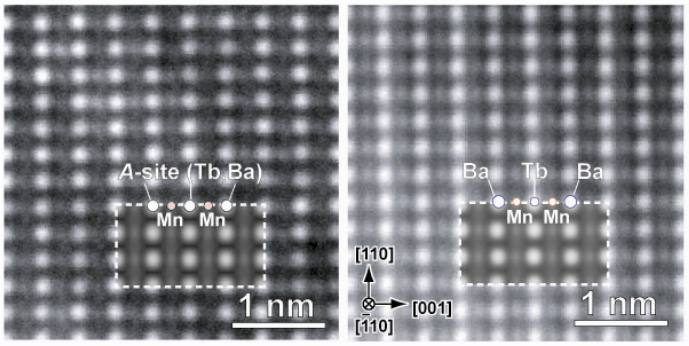

Fig. 5. High SN-ratio ADF images of disordered and ordered $Tb_{0.5}Ba_{0.5}MnO_3$. Insets show simulation results.

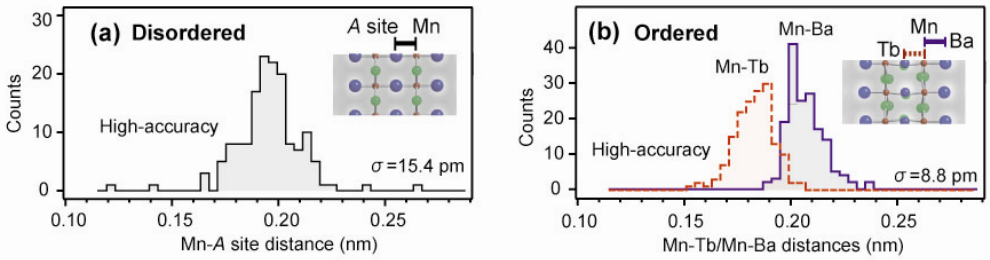

Fig. 6. Histograms of interatomic distances measured from the experimental ADF images (Fig. 5). (a) Interatomic distance between A-site and Mn-site in disordered phase. (b) Interatomic distances of Mn-Tb and Mn-Ba in ordered phase.

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