Mapping of atomic-site-specific oxidation states of metal atoms by EELS using STEM-moiré method.

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In STEM, two-dimensional moiré pattern can be obtained with controlled pixel interval whose pitch corresponds to the spacing of multiple of lattice fringes of the sample. Recently, we reported the pseudo atomic column elemental map using this STEM Moiré method [1]. An advantage of this method is low dose because a pixel interval is 10 to 20 times longer than that in conventional atomic column elemental mapping [2]. With such a sparse pixel interval, average dose density on a sample is drastically reduced to 1/100 or less than in the conventional method. With this method, we have already succeeded in observing a pseudo atomic column elemental map for a fragile mineral sample such as Aquamarine [3]. In that experiment, we used a pixel interval 100 times as long as in conventional method by utilizing 4x 4 super unit cells. Thus, this method is adequate for observing fragile samples or fragile atomic states. In this paper, we tried to visualize the difference of valence state of Mn atoms. In the sample of Mn_3O_4 [100], atomic columns of Mn^{2+}, Mn^{3+} and O^{2-} are observed in distinguished atomic columns. Difference of the oxidation state was detected by an atomic resolution EELS mapping reflecting ELNES (energy-loss near edge structure) structure, which was already reported previously [4].

In this work, samples of 50-nm-thick Mn_3O_4 were sliced from a resin block including the sample powder by microtome. The experiments were performed by an aberration corrected microscope (JEOL JEM-ARM300F) equipped with a cold field emission gun and Cs correctors.

Figure (a) shows a single crystal grain of Mn_3O_4. The STEM moiré pattern of HAADF signal from green rectangle in (a) is shown in (b). The left and right panels in (d) show EELS spectra of O-K and Mn-$L_{2,3}$. The structure of Mn-$L_{2,3}$ edge changes its shape depending on the atomic site. The colors of these spectra correspond to the color-masked atom sites in (b). The obtained EELS maps corresponding to colored ROIs in the spectra in (d) are shown in (e-g). The energy ranges for these maps are 531.5 - 554.6eV for O^{2-}, 642.3 - 645.2eV for Mn^{2+}, and 645.4 - 648.2eV for Mn^{3+}. The (h) shows an overlay map. The conditions that the number of pixels of the map was 32x32, the dwell time was 0.1 sec/pixel, the probe size and current were 0.1 nm and 90 pA, were used for our experiments.

The site specific valence numbers of Mn atoms, Mn^{2+} and Mn^{3+} were visualized by STEM moiré method in (e) and (f). We can conclude that STEM moiré method is usable for mapping of oxidation state of metal atoms. This result leads that we can try the atomic state mapping by this STEM moiré method even for very fragile samples.

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[2] E. Okunishi et al, Microsc. Microanal. 12 (S2) (2006) 1150.
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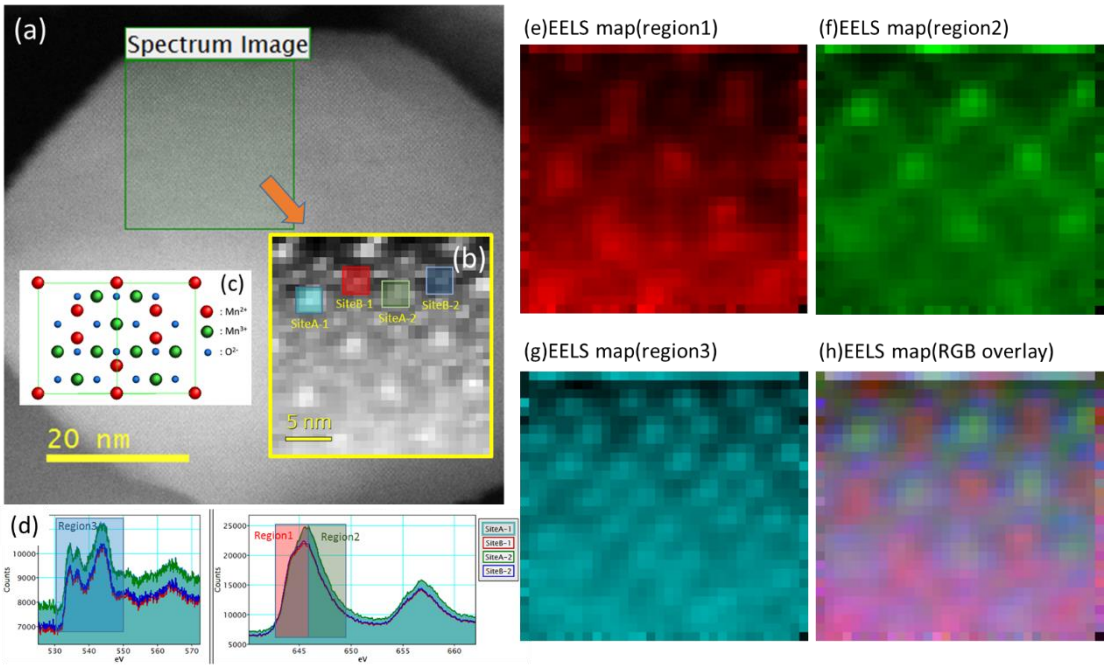

Figure. Mapping of a single crystal of Mn_3O_4 by STEM moiré method.