Atomic Resolution EDS Mapping in Oxide Materials

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Oxide materials have been used in many technological applications due to their superior mechanical and electronic properties. To understand the origin of these superior properties in oxide materials, it is necessary to identify the structures of the light elements in addition to the heavy elements inside materials even down to the atomic dimensions [1]. In this study, we demonstrate that all elements of an oxide material were identified by atomic-resolved energy dispersive X-ray spectroscopic (EDS) mapping. The analysis was achieved by using a scanning transmission electron microscope (STEM) equipped with a large area type of Si drift detector (SDD) and a spherical aberration corrector. Sensitivity of the SDD is improved at light elements as compared with the conventional Si (Li) detector, and thus atomic-resolved mapping using SDD-EDS has benefits for visualizing light elements even where heavy elements coexist. SDD-EDS mapping can become even more robust for determining the atomic sites when combined with the existing methods of Z-contrast and/or electron energy-loss spectroscopy (EELS).

Atomic-resolved EDS spectral images were acquired with an aberration corrected JEM-ARM200F STEM (cold-FEG) (JEOL, Ltd.) with 100 mm^2 SDD, operated at 200 kV. The spectral image was acquired from $BaTiO_3$ at the [001] zone axis with a convergence angle of 24.7 mrad and a probe current of about 200 pA to enhance the X-ray signals. X-ray peak separation analysis was performed on a raw data by using a commercial analyzer (Thermo Fisher Scientific Inc.). The S/N ratio of each image was improved by averaging over repeating units by the pattern matching method.

FIG. 1 shows atomic-resolved STEM EDS maps and STEM images of a $BaTiO_3$ single crystal. As usual, the main peaks of the Ti K lines (4.508 keV) and the Ba L lines (4.465 keV) are too near to be trivially separated on the spectrum in terms of the energy resolution in EDS. However, after the peak separation analysis undertaken in this study, the Ba and Ti column positions correspond well with the structure as given by the HAADF image. Furthermore, in the O K line map of FIG. 1c it is clear that high intensity consisting of the O K line signal was localized of the sites corresponding to the position of oxygen atoms as shown in the structure model. In $BaTiO_3$ viewed along the [001] direction, oxygen is present in both Ti-O mixture columns and pure O columns, with the same number density of oxygen atoms in both types of column. However, the oxygen EDS signal in the Ti-O column was slightly higher than that in the pure O column. This is because there is a difference in channeling (scattering) of the electron along the different columns [2]. To undertake quantitative analysis using EDS mapping, it is necessary both to have sufficient signal intensity and to account for the channeling

effect using a structure model and image simulation [3]. To identify the elements at each site as needed for elucidating microstructure into the future, the multi-dimensional analysis method involving the complementary combination of analytical electron microscopy of EDS and EELS will become more and more important.

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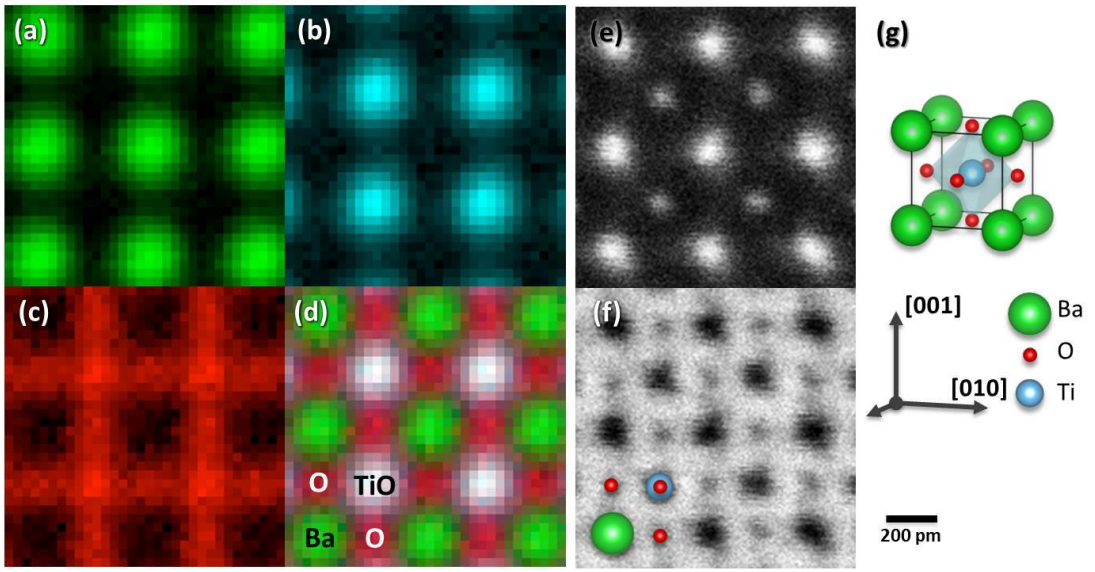

FIG. 1. An overlapped atomic-resolved EDS mapping (d) obtained from the separated peak signals of Ba L line (a), Ti K line (b) and O K line (c). Corresponding images of HAADF-STEM (e) and ABF-STEM (f) of $BaTiO_3$ viewed along [001] direction. Each of the atoms as shown in the structure model (g) is superimposed on (f).