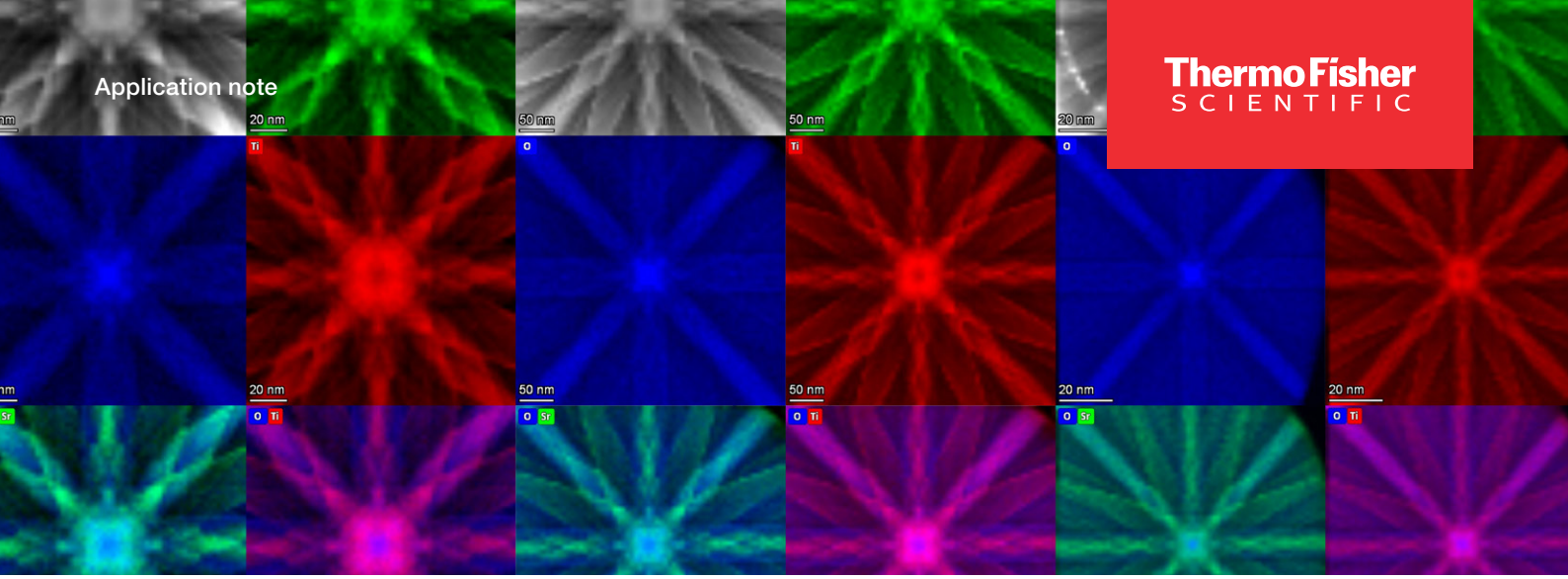

Analyzing beam-sensitive crystal structures with automated rocking beam XEDS

Introduction

Automation and advanced, customizable software have the potential to greatly expand the insights electron microscopy provides for materials science. Scripting in particular allows you to explore new scientific ideas through unique techniques and experimental workflows that are not easily accessible with commercial software. For this reason, Thermo Fisher Scientific has expanded the availability of Thermo Scientific™ Autoscript™ Software (previously for focused ion beam scanning electron microscopes) to transmission electron microscopes (TEMs). In TEM Autoscript Software, specific application programming interfaces (APIs) can control the optics, apertures, and detectors of the TEM, enabling new automated workflows in a Python environment.

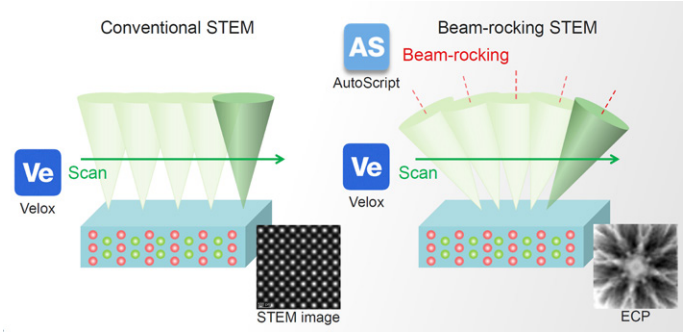

Figure 1. Comparison of compositional mapping and rocking beam techniques. In mapping, the beam is moved across the area of interest (A) while in rocking beam mode the stationary beam is tilted in both directions on the specimen (B).

In this application note, Python scripts are used to enable rocking beam channeling and energy-dispersive X-ray spectroscopy (XEDS) mapping on a Thermo Scientific™ Talos™ F200 TEM.[1-2] The higher collection efficiency of modern XEDS detectors enables a number of novel analyses of mixed columns in crystalline materials, including low-dose occupancy in beam-sensitive materials and the detection of low-concentration dopant atoms.

Methods

Atom-sized probes for scanning electron microscopy (STEM) offer unprecedented levels of sensitivity combined with low damage, enabling atomic-resolution compositional analysis and chemical mapping. STEM-XEDS uses relatively high electron-beam dosing, however, making it challenging to analyze beam-sensitive materials. Atom location by channeling-enhanced microanalysis (ALCHEMI) is an alternative method for the determination of atom-site-specific information on crystal composition.[3] In ALCHEMI, a parallel beam is rocked over a large sample area, resulting in a large excited volume with an increased detection limit or a minimized dose. This makes rocking beam beneficial for beam-sensitive materials (e.g., lithium-battery materials) or those with low-concentration dopants. Figure 1 illustrates these two methods; atomic-resolution compositional mapping is a standard functionality of Thermo Scientific™ Velox™ Software while rocking beam requires a combination of Velox Software and python scripting in Autoscript Software (Figure 2).

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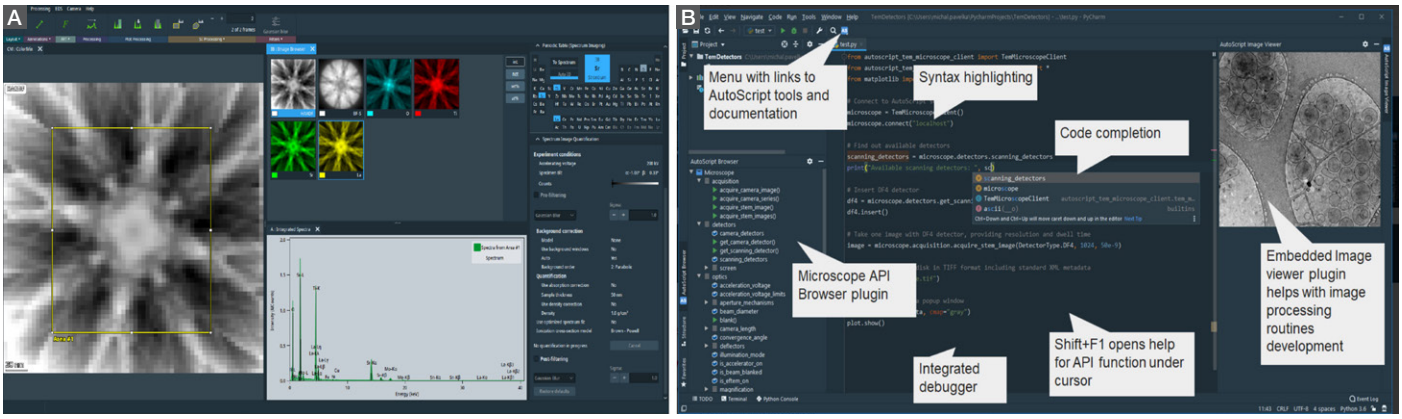
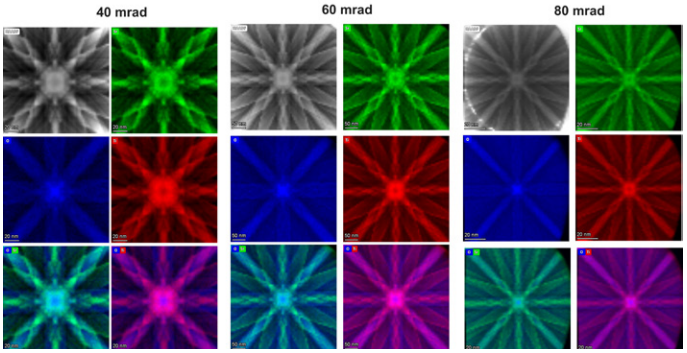


Figure 2. Graphical user interface of a) Velox Software and b) Autoscript Software. STEM detector and XEDS data is displayed and analyzed in Velox Software while experimental parameters are defined in Autoscript Software.

Performance

The available tilt range of the rocking beam method was verified on $SrTiO_3$ in (100) projection (Figure 3). The XEDS spectra provide ionization channeling pattern (ICP) information while the HAADF detector captures the electron channeling pattern (ECP) signal. Step size, number of tilts, and tilt range can be selected in the scripting environment, while the full spectra are analyzed with Velox Software. Background and deconvolution techniques in Velox Software were applied to the raw datasets to display net intensities. In these experiments, the illuminated areas were approx. 100 nm^2, but even smaller areas can be used, depending on the TEM platform. While a Talos F200X TEM with a Super-X Detector was used in this application note, the script is platform independent and can be run on a Thermo Scientific™ Spectra™ or Themis™ TEM with any Thermo Scientific XEDS detector (i.e., Super-X, Dual-X, or Ultra-X detector) and a control PC with Microsoft Windows 10 or higher.



HT	200 kV
Aperture	20 µm (C2)
Probe current	0.6 nA
Dwell time	250 ms
Image size	64x64 px
Acquisition / Frame	20 min / 1
Display	**Net**

Figure 3. Three rocking beam maps of $SrTiO_3$ in (100) projection, produced with different tilt ranges (i.e., half angles of 40, 60, and 80 mrad, respectively). These maps illustrate the maximum tilt range (top and middle images). The intensity ratio maps of the Sr/O and Ti/O ICPs (bottom images) reveal the elemental ratio changes with different beam-to-crystal orientations, which can influence quantitative compositional analysis.

Lanthanum doped $SrTiO_3$

SrTiO3 was doped with lanthanum to determine the ability of the rocking beam method to capture scarce dopant atoms. The XEDS results show the net counts determined with post-processing in Velox Software (Figure 4). The lanthanum ICP shows good agreement with the strontium ICP. The deconvolution function of Velox Software was able to separate the TiK and LaL edge intensities, resolving the overlap between LaL and TiK peaks in the XEDS spectra. These results indicated that the doped lanthanum is located mainly on the strontium sites (and not the titanium sites). Additionally, X-ray intensity minima in the strontium and titanium signals, as well as the maxima of oxygen at zero-tilt, illustrate the electron channeling effect, which makes effective quantification difficult on the zone axis. These results can help to prevent quantification errors by reliably identifying such effects.

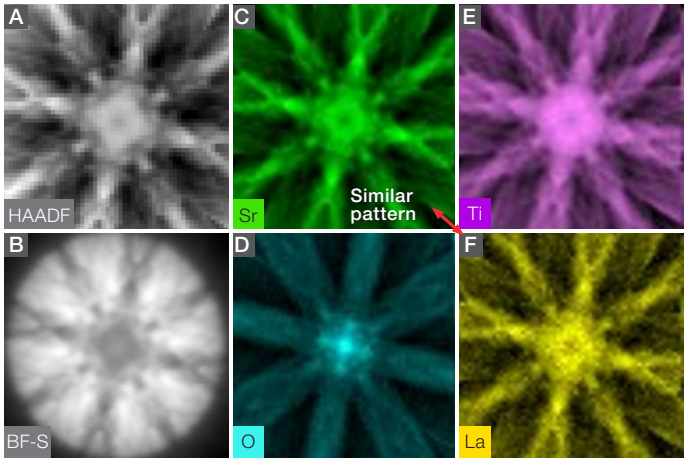


Figure 4. Electron channeling patterns (ECP) taken with a) the HAADF and b) BF detector, respectively. c–f) X-ray ICPs for La, Sr, Ti, and O were recorded simultaneously.

Conclusions

Conventional STEM-XEDS with atom-sized probes is capable of determining atomic-resolution compositional information, but requires a relatively high electron-beam dose. The rocking-beam ALCHEMI method is a highly sensitive, alternative approach that can accurately determine the location of atoms in a crystal's atomic columns with a much lower electron-beam dose. In this application note, TEM Autoscript Software was used to create a custom rocking beam method for Thermo Scientific transmission electron microscopes. This Python-based script enabled the collection of high-quality XEDS data on the structure and dopant-location in a beam-sensitive crystalline material. Such customizable analytical methods, enabled by a combination of high-quality detectors and scriptable software, are expanding the capabilities of XEDS, providing atomic-resolution chemical insights to drive advances in batteries, metal-organic frameworks, and low-doping materials.

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