VIP STEM Imaging

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Direct Imaging of the MoVTeNbO M1 Phase Using An Aberration-Corrected High-Resolution Scanning Transmission Electron Microscope**

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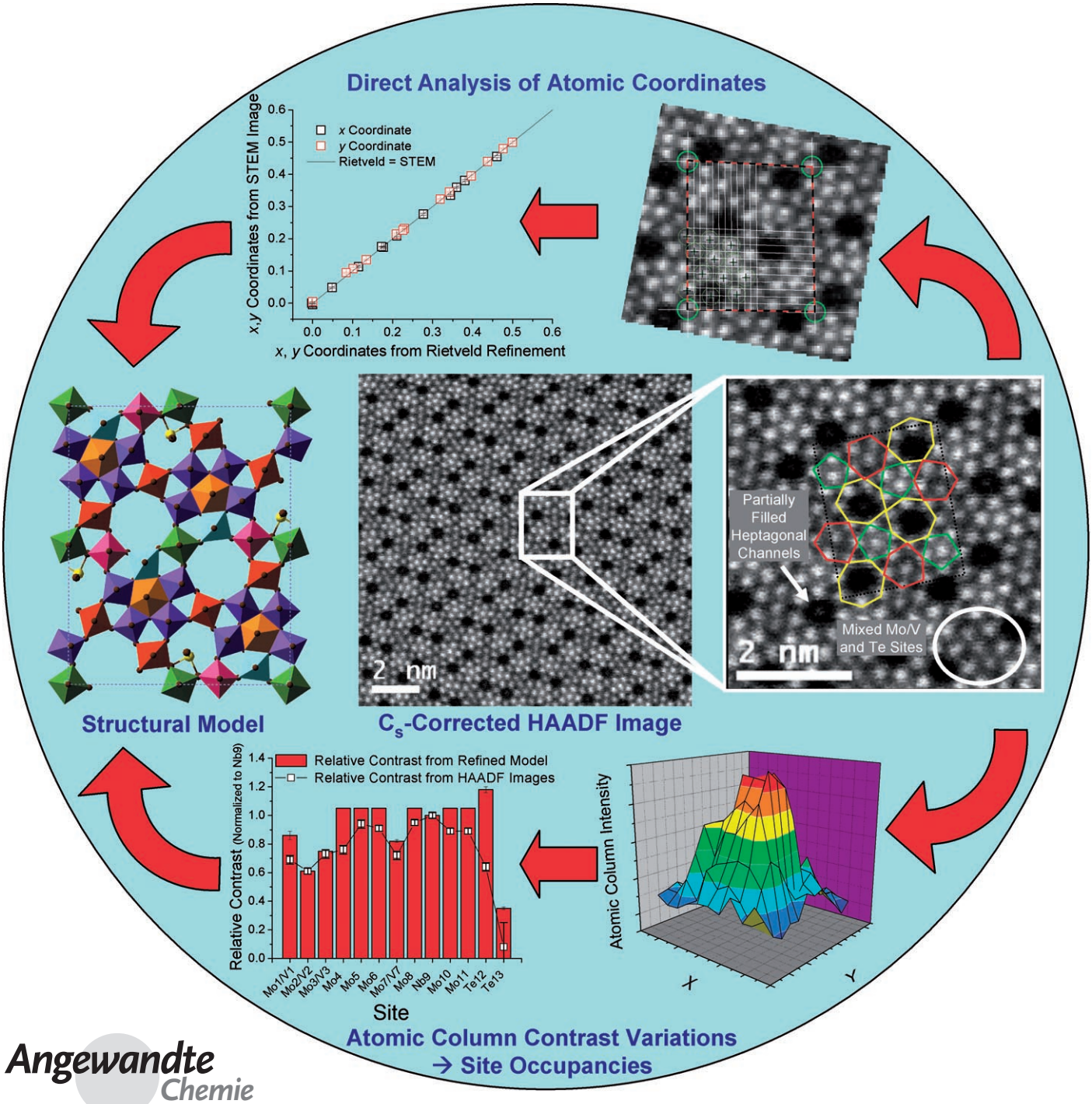
Dedicated to Professor Sir John Meurig Thomas on the occasion of his 75th birthday



Selective oxidation catalysis is crucial to society, resulting in about 25% of all important organic chemicals and intermediates used to make consumer and industrial products.[1] The development of new and improved catalysts for C2–C4 conversions is driven by the desire to replace existing olefin-based processes with cheaper paraffin-based ones. For the selective oxidation and ammoxidation of propane, several families of vanadium-containing oxide materials, such as the Al-Sb-V-W-O system,[2] the Mo-V-W-O system,[3,4] the Mo-V-Nb-Sb-O system,[5–7] and the Mo-V-Nb-Te-O system[8–12] have been identified as promising catalysts for acrylic acid and acrylonitrile production, respectively.

Perhaps the most promising of these catalysts is the two-phase Mo-V-Nb-Te-O system, also commonly referred to as the M1/M2 system.[10,13] This composite system is both active and selective with acrylonitrile yields of up to 62% in the case of propane ammoxidation.[13] A detailed model for the M1 structure, with the composition $\{TeO\}_{0.94}\cdot(Mo_{7.8}V_{1.2}Nb)O_{28}$, based on a simultaneous Rietveld refinement of high-resolution X-ray and neutron powder diffraction data has been reported.[10] The {TeO} entities are intercalated into channels formed by rings of corner-shared transition-metal octahedra. The extent of Te intercalation is sample dependent, and arguments persist over whether Te is restricted to the hexagonal channels[14] or also present in the heptagonal channels.[9,10]

The difficulty plaguing the structure refinements of such complex materials is that the models may have up to approximately 200 adjustable parameters, requiring high-quality diffraction data and a suitable starting model with imposed constraints to ensure a stable and converging refinement. Herein, we use an aberration-corrected[15,16] JEOL2100F TEM operated in STEM mode to independently obtain a model for the M1 structure and compare it to the one determined by DeSanto et al. (Figure 1b).[10] It has been shown that using aberration correction allows imaging at sub-Ångstrom resolution.[17] This procedure has the potential to provide significantly improved starting models of complex inorganic structures which can subsequently be used in Rietveld refinements.

The high-resolution high-angle annular dark-field (HAADF) image in Figure 1b shows an M1 crystallite oriented along the [001] direction. The highlighted regions in the HAADF and bright-field (BF) STEM images in Figures 1c and 1d show that the hexagonal and several of the heptagonal channels are occupied. The partial occupancy of Te in the heptagonal channels is consistent with the Rietveld model predicting approximately 20% occupancy. A rendering of the unit cell based on the Rietveld model was scaled with a constant aspect ratio and superimposed on the HAADF image shown in Figure 1e. Good qualitative agreement between the superimposed unit cell and the HAADF image is observed.

A quantitative comparison of the *x*,*y* coordinates derived from the HAADF image with the Rietveld model is depicted in Figure 2. In the [001] projection, the structure has only a single polyhedral layer repeat ($c = 4.02$ Å), that is, there are no overlapping crystallographically distinct metal sites. This allows for the direct extraction of *x* and *y* atomic coordinates from the HAADF images. These coordinates were determined by placing a grid across the unit cell and allowing for the compensation of distortions introduced by sample drift and the rastering of the electron beam across the sample. The comparison of the HAADF-based *x*,*y* coordinates with those from the Rietveld-refined model reveals good agreement, with discrepancies in atomic positions that are less than 0.3 Å.

For thin samples, a major advantage of using high-resolution HAADF imaging is that to a first approximation, the image contrast scales with the square of the atomic number (Z).[18] Comparison of the expected contrast ratios from the refined M1 model and HAADF images is presented in Figure 3.[19] Most of the measured intensities follow the trends in the site occupancies predicted by the Rietveld model. The deviations include a low Te occupancy in the HAADF model owing to partial sublimation during exposure to the electron beam, and lower contrast for the Mo4 site, suggesting that there may be some vanadium present. The Mo/V1 site and the pentagonal-ring sites also have HAADF contrast that is slightly low relative to the Rietveld model. Efforts are currently underway to simulate these HAADF images and to better scrutinize the site occupancy discrepancies.

The agreement of the Rietveld-based model with the STEM images is encouraging and has important implications for the analysis of such complex inorganic structures. Our refinement of diffraction data from the M1 phase took nearly two years to complete owing to limitations in the starting model. That model was based on: 1) the unit cell symmetry and estimated lattice parameters from selected area electron diffraction (SAED), 2) the relative elemental compositions from energy-dispersive X-ray spectroscopy (EDS) and starting precursor ratios, 3) vague estimates of atomic positions from non-aberration corrected bright-field high-resolution images (which at the time showed complete absence of Te in the channels owing to sublimation by the electron beam), and 4) an estimate of the concentrations of the possible residual impurity phases (such as M2 and Te^0).[10] Procedurally,

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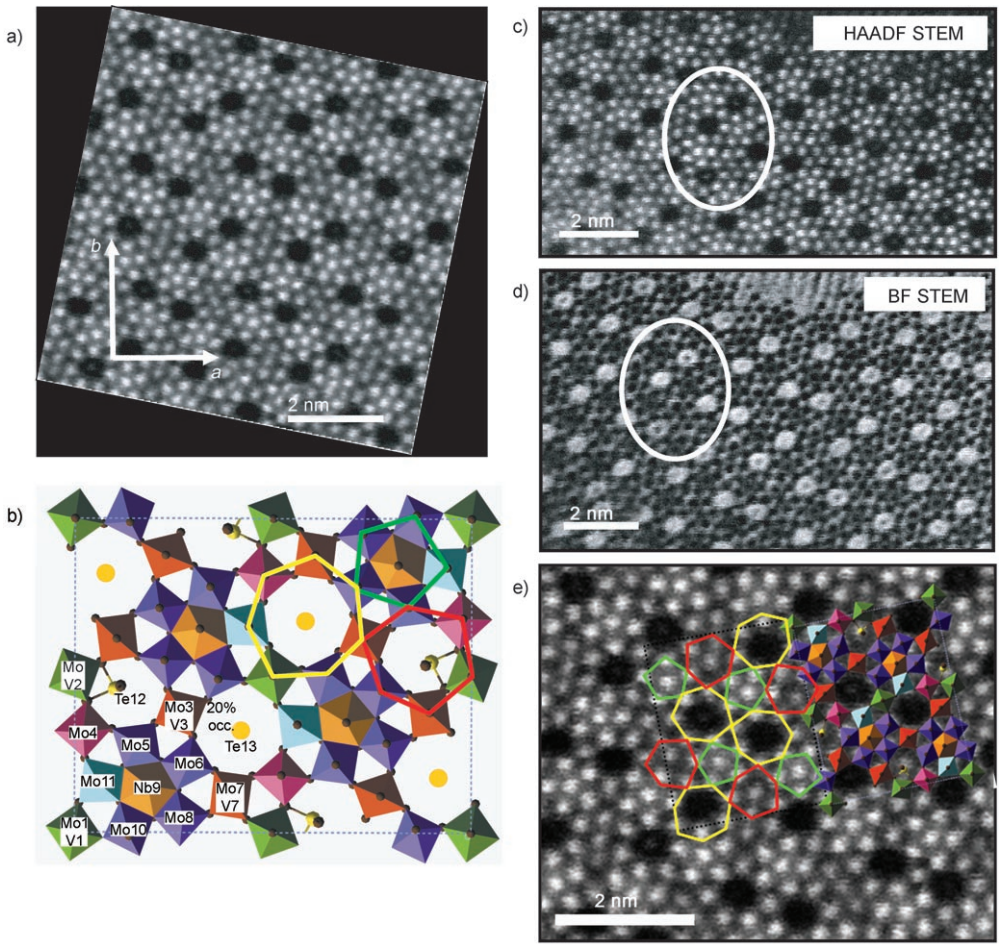

Figure 1. a) high-resolution HAADF STEM images showing the [001] projection of the M1 phase b) Rendering of the model M1 structure from simultaneously refined powder X-ray and neutron data proposed by DeSanto et al.[10] Full model details are published in reference [10], c) high-resolution HAADF STEM image showing areas with occupied heptagonal channels within the white oval, d) high-resolution BF STEM image of the same area showing the same filled heptagonal channels, e) magnified portion of the [001] projection showing a scaled model unit-cell superimposed on the high-resolution HAADF STEM image. Note that the images have not been processed or altered.

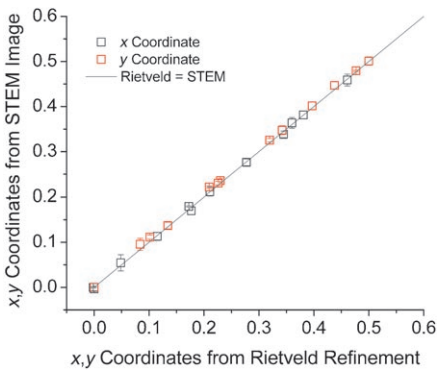

Figure 2. Plot showing the fractional coordinates of the refined model plotted against the experimentally determined coordinates measured directly from raw high-resolution HAADF STEM images. Note that the error bars are small compared with the plot symbols.

approaching the analysis by starting with aberration-corrected HAADF images, SAED patterns, and EDS data would provide a significantly improved starting model for the subsequent Rietveld analysis and reduce the extent of "trial-and-error" iterations. Such a strategy would provide a preliminary symmetry, estimates of lattice parameters and atomic coordinates for the high-atomic-number (high-Z) atoms, and would give indications of likely site occupancies (provided appropriate simple projections with little or no overlap of atoms can be found). Additionally, the low-Z sites (oxygen in this case) can be modeled using typical bond lengths and valences. Such a high-quality starting model should significantly reduce the time required to solve complex inorganic structures.

To summarize, aberration-corrected STEM imaging was used to directly observe the M1 metal framework in the [001] projection. The structural model proposed previously by DeSanto et al.[10] was found to be largely consistent with our STEM measurements in terms of the intercalation of Te in both the hexagonal and heptagonal channels, atomic positions, and site occupancies. Efforts are underway to simulate the HAADF images to further quantify the metal site occupancies. Furthermore, based on the HAADF results, we will revisit the Rietveld analysis to test possible variations, such as evaluating possible V occupancy on the M4 site.

The ability to quickly and directly interpret HAADF images of crystallographic projections with minimal atomic overlap and thereby determine the fractional atomic coordinates to within 1% and the site occupancies to within 15% uncertainty could dramatically improve the quality of the initial structural models used in Rietveld refinement. This will increase the structural and chemical complexity of inorganic structures that can be solved by using "powder methods" alone. The significant acceleration of the structural characterization of powders would provide vital structural input for

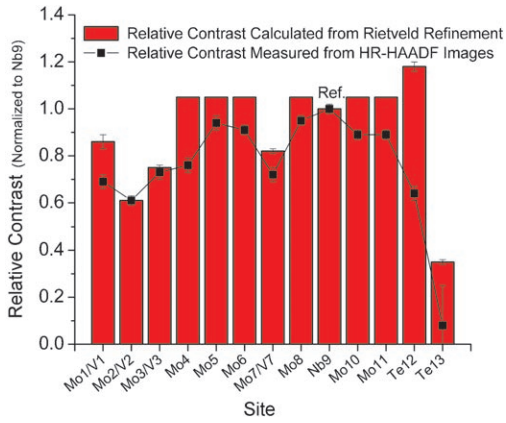

Figure 3. Comparison of occupancies derived from HAADF-STEM with those obtained by Rietveld refinement. Normalization is achieved with reference to complete occupancy of Nb in the Nb9 site. Discrepancies for the Te occupancies are expected owing to sublimation under the electron beam.

high-throughput screening in catalysis and other research areas.

Experimental Section

Nearly phase-pure samples of the M1 phase were prepared according to published methods.[10] The sample analyzed herein was the same as that in the studies completed by DeSanto et al.[9,10] HR-STEM was completed on a JEOL 2100F equipped with an aberration-corrector (from CEOS GmbH, Germany) on the illumination system. Geometrical aberrations were measured and controlled to provide less than a $\pi/4$ phase shift of the incoming electron wave over the probe-defining aperture of 14.5 mrad. HAADF STEM images were acquired on a Fischione Model 3000 HAADF detector with a camera length such that the inner cut-off angle of the detector was 65.6 mrad. The scanning acquisition was synchronized to the 60 Hz AC electrical power to minimize 60 Hz noise in the images and a pixel dwell time of 32 μs was chosen. Samples were prepared for TEM by grinding the as-prepared catalyst and dipping a holey-carbon-coated Cu grid into the powder.

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[19] We made the following assumptions when comparing the contrast observed in our HAADF–STEM images with expected values based on Rietveld-refined occupancies: 1) the observed intensities follow the Z^2 Rutherford scattering relationship, 2) within a unit cell, the thickness of the crystal was assumed constant, 3) scattering contributions from oxygen were only considered at positions superimposed in the [001] projection with the metal site columns, 4) a constant integration area was appropriate for all metal framework sites, and 5) the background was constant throughout the unit cell. Using these assumptions, the total intensity for each atomic column was calculated by integrating the individual pixel intensity from a constant region of interest for each framework site. The background from several empty heptagonal channels in the vicinity of the unit cell of interest was averaged and then subtracted from the integrated intensity of each site. The raw intensities were then normalized to the Nb9 site where complete occupancy by Nb was assumed; any partial occupancy of Mo in this site would have minimal influence on the results since they are nearest neighbors in the periodic table.

