Exploring Surface Phenomena with TEM and STEM

Roei Broneschter[1], Yaron Kauffmann[1], Klaus Van Benthem[2], Wayne D. Kaplan[1]
[1] Department of Materials Science and Engineering, Technion, Haifa, Israel
[2] Department of Materials Science and Engineering, University of California, Davis, CA

Introduction

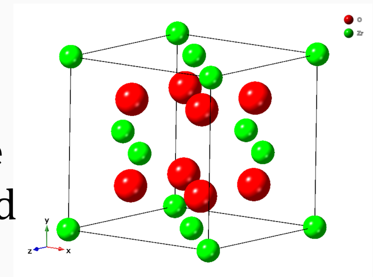


Figure 1: bulk structure of YSZ

- Yttria stabilized zirconia (YSZ) is a cubic ceramic material mainly used in solid oxygen fuel cells (SOFC). YSZ has the fluorite structure (figure 1).
- The surfaces of a material are planar defects with excess energy, and the 2-D structure may differ from that of the bulk. Surfaces of conducting materials can be characterized using scanning tunneling microscopy (STM) which is challenging or impossible for insulators such as most ceramics.

  To characterize ceramic surfaces, electron microscopy can be used.
- In TEM mode micrographs are not directly interpretable, but by using optimal negative C_s imaging (NCSI) conditions in HRTEM the micrographs have a bright-atom contrast and are directly interpretable[1]. In the multi-slice method scattered electron wavefunctions are simulated by interacting them with the projected potential of a crystal which was first "sliced" to a thickness of ~2Å. In this work the EMS software package was used for the multi-slice simulations[2].
- In scanning-TEM (STEM) imaging using a high angle annular dark field (HAADF) detector the intensity of the atom columns is proportional to Z^2 (the atomic number) . In integrated differential phase contrast (iDPC) mode the intensity is nearly linearly proportional to Z, allowing us to detect weak scattering atom columns (such as oxygen columns)[3].
- In this study the {111} surface of YSZ was characterized using all the mentioned EM techniques **implemented together**.

Experimental

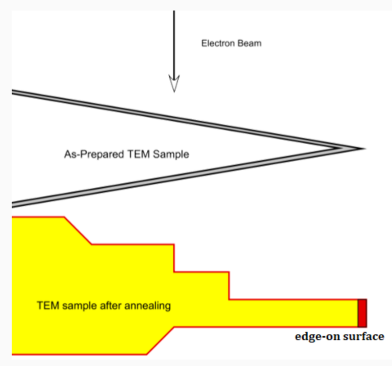


Figure 2: Schematic drawing illustrating the faceted sample after annealing

- A $8\%_{mol}$ Y_2O_3 *doped* ZrO_2 (YSZ) polycrystalline sample was made by uniaxial pressing and sintered at 1400°C for 4h in air. A conventional TEM sample was made and annealed for 1 minute at 1000°C to remove amorphous layers by faceting the edge of the sample (figure 2).
- The FEI-TITAN was used to acquire micrographs from the same area in TEM and STEM including HAADF and iDPC.
- For the HRTEM analysis aberration correction mode and a negative C_s coefficient of $-7\mu m$ was used. The NCSI condition for $C_s = -7\mu m$ was an over-focus of $\Delta f = +6nm$.

  By acquiring a focal series and using HR-DIMA software on unfiltered micrographs the defocus value for each micrograph (40 micrographs) and the thickness of the sample were found. The accuracy of the HRTEM micrographs was found by simulations using the multi-slice method.
- STEM micrographs of the same sample were acquired both in HAADF and iDPC to compare with the TEM data and fully characterize the {111} surface of YSZ.

Results and Discussion

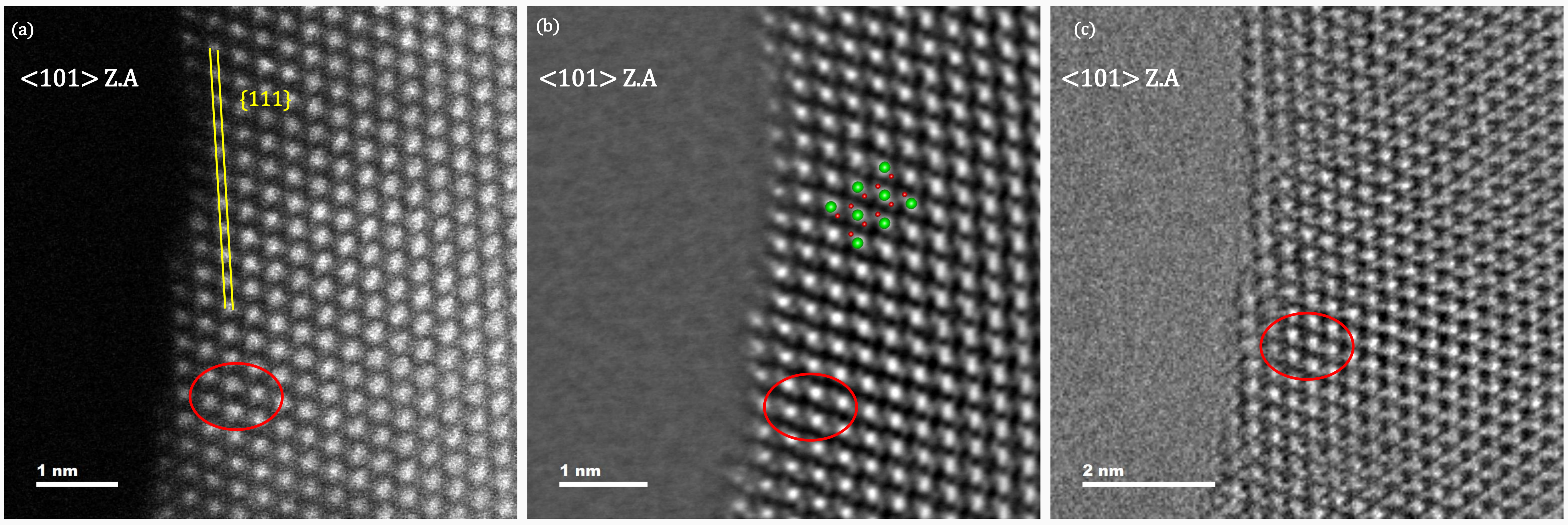


Figure 3: Micrographs showing the same area of YSZ in a zone axis (ZA) [101] and a thickness of ~2 unit cells acquired in: a) HAADF mode (STEM), b) iDPC (STEM) c) Negative C_s HRTEM. All micrographs are unfiltered. In figure 3b a simulation of the YSZ lattice in a [101] ZA was superimposed on the micrograph to show the positions of the atom columns (Zr in green and oxygen in red). A possible reconstruction of the top and bottom surfaces in which the oxygen columns have a slight displacement relative to the bulk structure can be observed in fig 3b, this needs further analysis. Figure 3c was taken at a defocus of $\Delta f = +17nm$ which is not at the optimal NCSI conditions with XCC metric of 0.73 compared to a simulated perfect lattice. A step at the surface can be seen in all three micrographs According to the iDPC micrograph the {111} edge-on surface is oxygen terminated, as expected after annealing in air. Also in all micrographs a lattice bending near the surface step was detected (marked with a circle) correlating to a change in d-space of ~10%. This is the first time to the best of our knowledge that the same area was imaged in three different modes of operation of S/TEM.

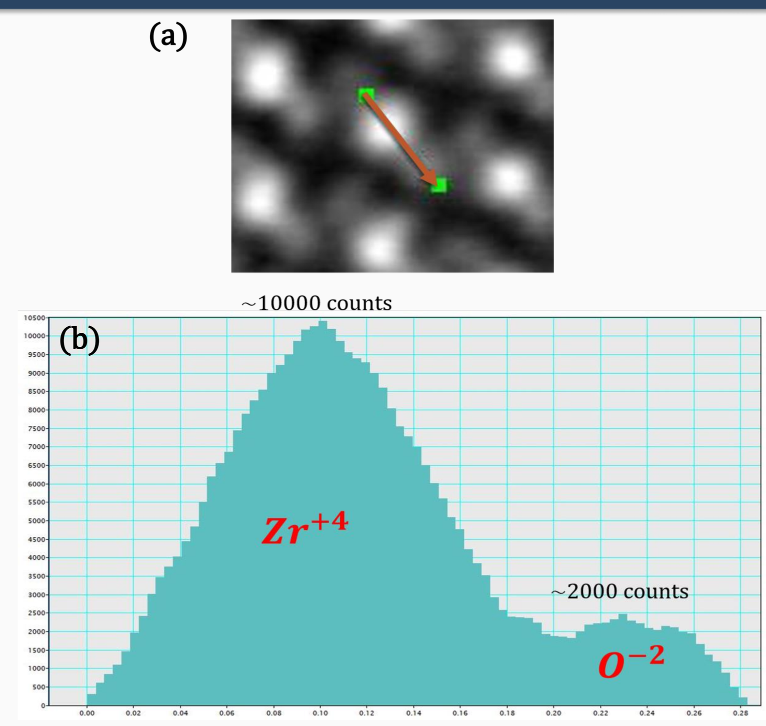
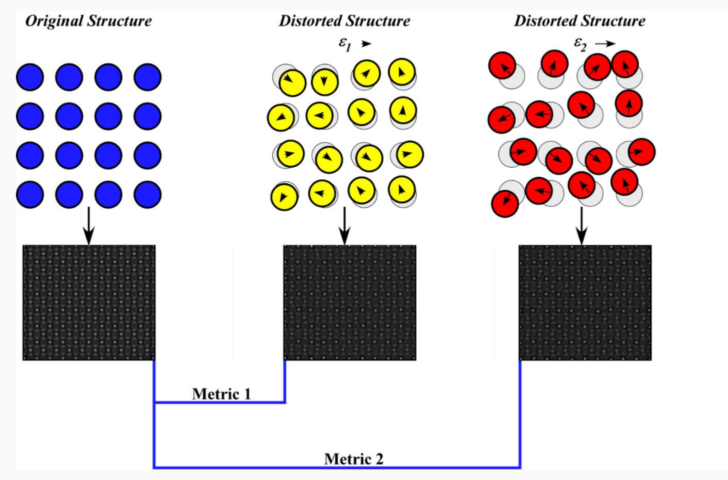


Figure 4: a) iDPC micrograph from a [101] ZA of YSZ (section from figure 3b) showing contrast from both Zr columns and Oxygen columns. b) line-scan of a Zr-O columns pair showing intensity ratio of ~0.2 which correlates to the atomic number ratio of zirconium (40) and oxygen (8). If the image was taken in HAADF mode the intensity ratio would be 0.04, making oxygen columns detection almost impossible due to the signal to noise ratio.



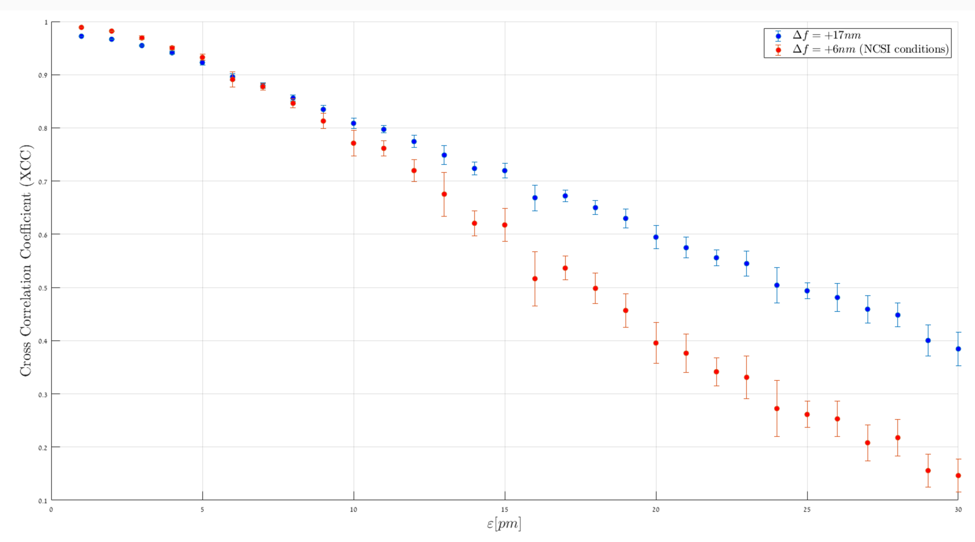


Figure 5a) Schematic illustration of the accuracy analysis using the multi-slice method, simulating a perfect crystal and moving each atom column in a random direction 25 different runs at different displacement values from 1pm to 30pm[4]. Images of the simulated crystal (with column displacements) were compared to the original using the cross-correlation coefficient (XCC) metric with XCC=1 being a perfect match, meaning no difference between the 2 images. 5b) XCC values as a function of displacement for $\Delta f = +6,17nm$ corresponding to the HRTEM micrographs of figure 3c and 6a which gives the micrographs an accuracy of 14pm for 3c and 13pm for 6a (which is the optimal NCSI).

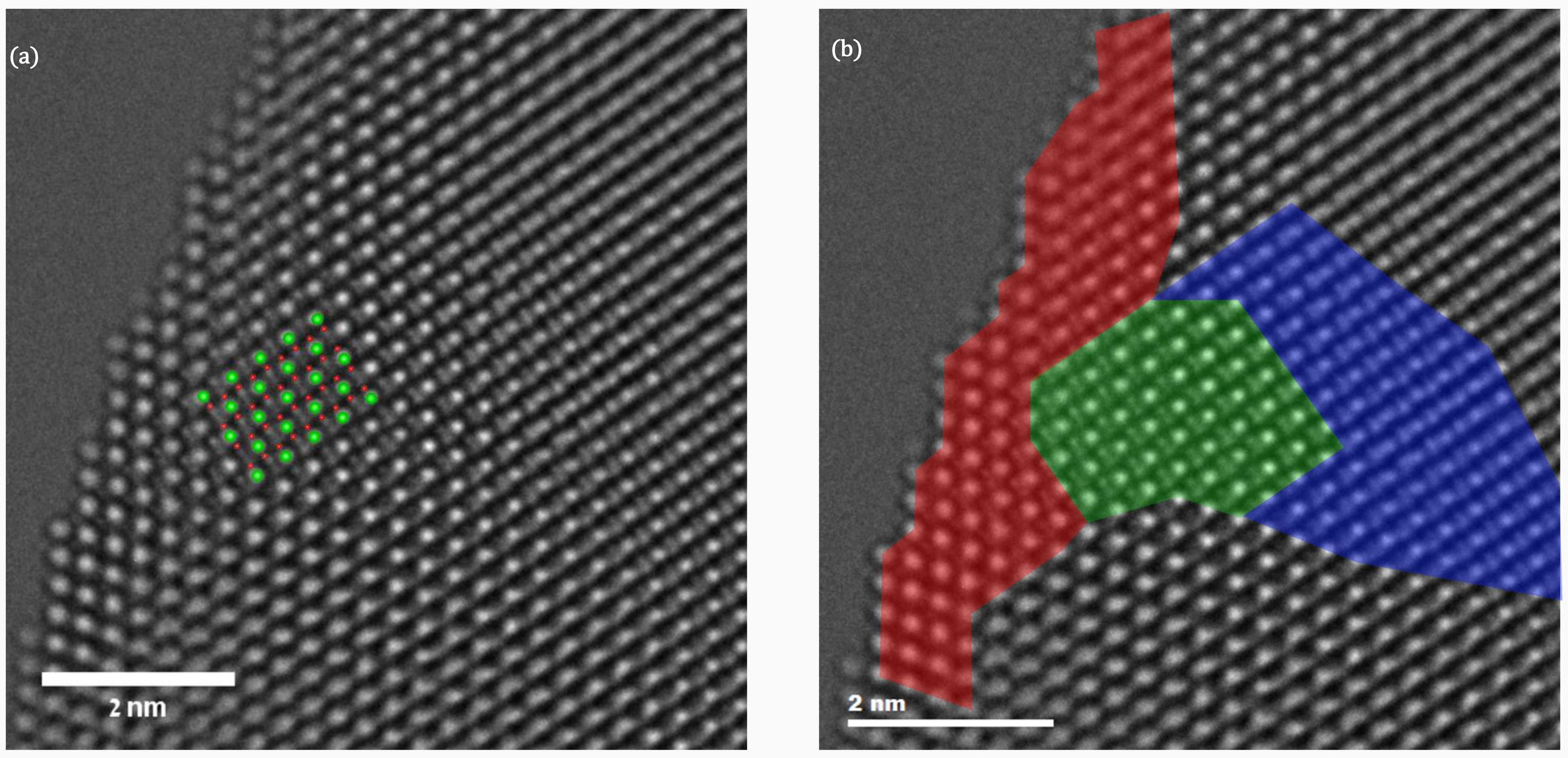


Figure 6a) A different area of the same grain as in figure 3 taken in TEM mode with $C_s = -7\mu m$ and $\Delta f = +6nm$ with an XCC value of 0.67 compared to a simulated image with the same conditions (not shown here) . Like in figure 3b a simulation of YSZ lattice in [101] ZA was superimposed on the micrograph to show the positions of the atom columns. It is important to note that this is an unfiltered HRTEM micrograph that is directly interpretable due to being at the optimal NCSI condition. 6b) A thickness map of the area, which was made using the help of the DIMA software under the assumption of the same structure and defocus value across all the region. The thickness varies between different regions in the sample and are marked as follows: 1 unit cell in red, 2 unit cells in green and 3 unit cells in blue. It's worth noting that oxygen column detection can vary with the thickness of the sample, and not only with the defocus, as mainly seen in figure 6a.

Summary & Conclusions

- Weakly scattering atom columns can be detected in both STEM (iDPC) and TEM (NCSI).
- All three imaging modes showed a change in the d-space due to lattice bending near a surface step.
- Using iDPC it is possible to detect the oxygen termination of {111} surfaces in YSZ.
- Thickness variation affects oxygen detection when using negative C_s.
- The accuracy of HRTEM micrographs can be determined using simulations, and here it was found to be around 13-14pm.

Future Work: How much Top-Bottom relaxation/reconstruction can affect TEM image?

References:

1) Jia, Chun-Lin, et al. "High-Resolution Transmission Electron Microscopy Using Negative Spherical Aberration." *Microscopy and Microanalysis*, vol. 10, no. 02, 2004, pp. 174–184.,
2) Stadelmann, P.A. "Ems - a Software Package for Electron Diffraction Analysis and HREM Image Simulation in Materials Science." *Ultramicroscopy*, vol. 21, no. 2, 1987, pp. 131–145.
3) Lazić, Ivan, et al. "Phase Contrast Stem for Thin Samples: Integrated Differential Phase Contrast." *Ultramicroscopy*, vol. 160, 2016
4) Kauffmann, Yaron, et al. "The Accuracy of Quantitative Image Matching for Hrtem Applications." *Materials Characterization*, vol. 54, no. 3, 2005, pp. 194–205.,