

**HAADF-STEM IMAGING: FROM A QUALITATIVE TO A QUANTITATIVE INTERPRETATION OF ATOMIC-RESOLUTION HAADF-STEM IMAGES.** Miran Čeh(1), Sašo Šturm(1), Hui Gu(2) and Makoto Shiojiri(3). (1)Department for Nanostructured Materials, Jožef Stefan Institute, Ljubljana, Slovenia; (2)State Key Lab of High Performance Ceramics and Superfine Macrostructures, Shanghai Institute of Science, China; (3)Kyoto Institute of Technology, Kyoto, Japan. Email: miran.ceh@ijs.si

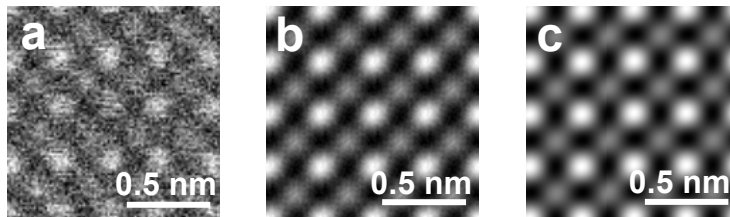
Atomic-resolution high-angle annular dark-field scanning-transmission electron microscopy (HAADF-STEM), also known as Z-contrast imaging, has become a promising technique to assess chemical information on the atomic scale. The HAADF-STEM images are recorded in a FEG (S)TEM with an annular detector at large inner angles. In this way the contribution of the Bragg reflections is minimized and incoherent thermal diffuse scattering (TDS) becomes the prevailing contribution to the image intensity [1,2]. Such incoherent STEM images are almost insensitive to defocus and/or thickness changes, and in contrast to HRTEM images, the atomic columns always appear as white dots. Since the intensity of TDS is related to the average atomic number,  $Z$ , of the atomic columns, a qualitative interpretation of HAADF-STEM images is relatively straightforward. A quantitative interpretation of HAADF-STEM images, however, requires image simulations and image matching [3]. In the present paper we show a few examples of qualitative and quantitative interpretations of atomic-resolution HAADF-STEM images.

In our work we investigated the  $\text{CaTiO}_3\text{-La}(\text{Mg,Ti})\text{O}_3$  solid solution,  $\text{KTiO}_2(\text{OH})$ ,  $\text{CaTiO}_3$  and  $\text{CaO}$ -doped  $\text{SrTiO}_3$ . The specimens for the HAADF-STEM observations were prepared by high-energy and/or low-energy ion milling and were observed in a FEG JEOL-2010F ( $C_s=0.48$  mm). The probe semi-angle was 10 mrad. The inner and outer annular angles of the HAADF detector were 100 and 220 mrad, respectively. The HAADF-STEM image simulations were carried out using a calculation scheme developed by Watanabe *et al* [4]. Atomic-resolution HAADF-STEM images usually exhibit a small signal-to-noise ratio. Additionally, they may also contain artifacts arising from the instabilities of the scanning unit or the environment. The processing techniques in reciprocal space using Bragg masks may not always be appropriate due to the high noise and the possible non-periodic details in the images. If the microscope conditions are stable, the signal-to-noise ratio can be improved by average filtering in real space, which can be additionally followed by polynomial processing (Figure 1). However, in cases when image distortions are significant, it is desirable to eliminate them prior to other processing by so-called image-warp processing, which repositions the intensities' maxima of individual atom columns in the HAADF-STEM image according to the structural model obtained by HRTEM [5]. A qualitative interpretation of atomic-resolution HAADF-STEM images is usually straightforward since the atom columns with the higher average atomic number,  $Z$ , always possess a higher intensity compared to the atom columns with the lower average atomic number,  $Z$ . Our observations confirmed that differences as small as 2% in the average atomic number,  $Z$ , can be detected by HAADF-STEM imaging. In a qualitative interpretation of atomic-resolution HAADF-STEM images one can compare intensity ratios between different atom columns or use intensity profiles to show the difference in the chemical composition between individual atom columns. In this way one can qualitatively interpret the ordering or partial ordering of solute atoms in bulk materials, evaluate the occupancy of atom columns in special structures, study the segregation of impurities along grain boundaries, etc. (Figure 2). A quantitative interpretation requires image simulations and matching of the processed experimental images with the calculated ones. However, in order to calculate HAADF-STEM images the exact structure should be known, i.e., the positions of the atoms, in order to create proper supercells for the calculations. Only when the exact structure is known can the HAADF-STEM image be calculated and matched with the experimental image. In figure 3 we show a processed experimental HAADF-STEM image of pure, bulk  $\text{CaTiO}_3$  in the  $[110]_{\text{CT}}$  zone axis, which was compared with the defocus-thickness series of simulated images until the best fit was found for a thickness of 35 nm and a defocus  $\Delta f=-20$  nm. HAADF-STEM

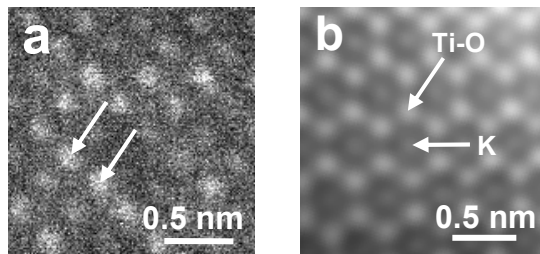
images of the  $\text{CaTiO}_3$  were calculated using Bethe's method, taking into account thermal diffuse scattering (TDS). The second example represents a quantitative HAADF-STEM analysis of a Ruddlesden-Popper-type fault in CaO-doped  $\text{SrTiO}_3$  (Figure 4). The comparison of the experimental and calculated intensity profiles across the atoms at the fault and in the bulk clearly show that Ca does not enter the solid solution but remains only at the fault. In the presented case the amount of Ca at the fault was 5 at%. It can be concluded that HAADF-STEM imaging is a very powerful analytical technique; however, it cannot replace HRTEM. HAADF-STEM and HRTEM are complementary and as such should be applied together in materials characterization at the atomic level.

### References

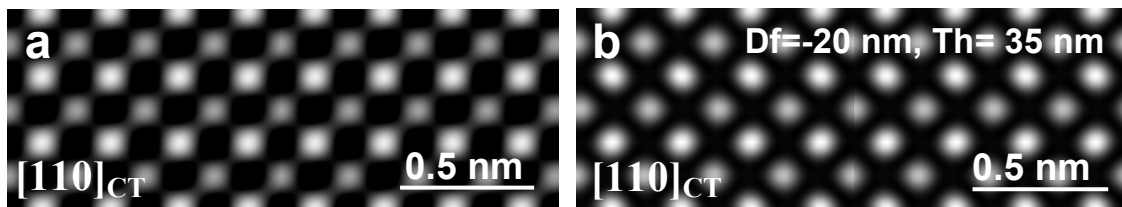
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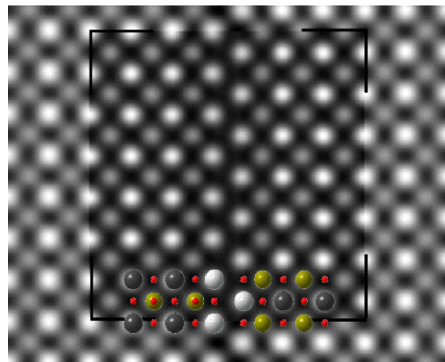
**Figure 1.** Processing of atomic-resolution HAADF-STEM images. (a) Experimental image, (b) average filtered image of experimental image, and (c) polynomial average filtered image.



**Figure 2.** (a) Experimental atomic-resolution HAADF-STEM image of  $\text{CaTiO}_3\text{-La(Mg,Ti)O}_3$  solid solution. Note uneven distribution and partial ordering of La atoms on A sites. (b) Processed HAADF-STEM image of  $\text{KTiO}_2(\text{OH})$  showing even distribution of K atoms in channels as viewed in the  $[0001]$  zone axis.



**Figure 3.** (a) Processed experimental atomic-resolution HAADF-STEM images of  $\text{CaTiO}_3$  in the  $[110]_{\text{CT}}$  zone axis with (b) the corresponding simulated image. Df-defocus, Th-thickness.



**Figure 4.** Processed experimental HAADF-STEM images of APB in CaO-doped  $\text{SrTiO}_3$ . The inserted parts represent a simulated image according to the structural model. The correlation between the calculated images and the processed experimental images is very good.

● O ● Ti ● Sr ● Ca<sub>0.95</sub>, Sr<sub>0.05</sub>