QUALITATIVE AND QUANTITATIVE INTERPRETATION OF ATOMIC-RESOLUTION HAADF-STEM IMAGES.

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Atomic-resolution high-angle annular dark-field scanning-transmission electron microscopy (HAADF-STEM) has become a promising technique to assess chemical information on the atomic scale. In HAADF-STEM images incoherent thermal diffuse scattering (TDS) is 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. It has been widely accepted that qualitative interpretation of HAADF-STEM images is simple and does not require image simulations and image matching, since the atom columns with higher average atomic number Z should appear brighter as compared to the atom columns with lower average atomic number Z. This may be true for many cases, however, in our recent HAADF-STEM studies of various materials we observed that local lattice distortions due to foreign atoms, defects, very small structural variations and also setting of the microscope, may affect the experimental intensities of atom columns in such a way that qualitative interpretation based on the atom columns intensities may be erroneous without images simulations. In our contribution we show results of HAADF-STEM imaging for bulk CaTiO₃ (CT) and Ba₂NaNb₅O₁₅ (BNN). In both materials the intensities of atom columns can be misinterpreted without comparison with the corresponding calculated images.

Figures 1a,b show processed experimental HR atomic resolution HAADF-STEM images of CT taken at what seems to be the same zone axis, since both images exhibit typical pattern as can be seen in the HRTEM along the [001] perovskite zone axis. Clearly there is a large difference in the intensity ratios between high intensity and low intensity dots in both experimental images. Such large difference could easily be attributed to different chemical composition of CT in both images. However, at room temperature CT crystallizes in a distorted perovskite structure (SG=Pbnm62) where TiO₆ octahedra and Ca atom columns are slightly displaced from positions in ideal perovskite. In order to determine the origin for different intensity ratios we calculated the defocus-thickness series for various CT crystal orientations producing cubic pattern and matched simulated images with the experimental images. The HAADF-STEM images were calculated using scheme developed by Watanabe et al [3]. The results showed that both images were taken at different zone axis and that difference in intensity ratios is not a consequence of variations in chemical composition (Fig. 1 c,d). This result could not be obtained without image calculations. Figure 2a shows the BNN tungsten bronze-type structure, as viewed along the [001] zone axis. This structure exhibits characteristic A1 sites filled with Na atoms, which are surrounded by four A2 sites filled with Ba. Each Ba atom is surrounded by 5 Nb atoms thus forming a typical array of squares and pentagons, which are marked in the images. The corresponding HAADF-STEM image, calculated for defocus value of -25 nm and specimen thickness 20 nm shows that for these conditions the Ba atoms exhibit the highest intensity and that not all A1 sites have the same intensity despite the same occupancy with Na atoms (Na*,Na) (Fig. 2b) [3]. Additionally, the Nb atom columns between adjacent Ba atoms exhibit higher intensity as compared to other Nb atom columns. The experimental HAADF-STEM image of BNN in the [001] zone axis (Fig. 2c) was filtered with Bragg mask in the FFT images. The processed experimental image (Fig. 2d) agrees well with the calculated images: the A1
sites have different intensities and the Nb atoms between adjacent Ba have higher intensity as compared with other surrounding Nb atoms. It should be stressed that both features could be easily misinterpreted without calculated image. Namely, the uneven intensity of A1 sites could be attributed to not fully occupied A1 sites, i.e. variations in the chemical composition, while the higher intensity Nb atom columns could be mistaken for Ba atom columns. What still needs further explanation is why the intensities of Ba atom columns are lower as compared to the intensities of Nb atom columns in experimental images. Our general conclusion is that HAADF-STEM image calculations are necessary for both, qualitative and quantitative interpretation of experimental images in order to avoid possible misinterpretation based on the variations in atom columns intensities only.

References

Figure 1. Processed experimental HR HAADF-STEM images of CaTiO$_3$ in (a) [110]$_{CT}$, and (b) [001]$_{CT}$ zone axis. The corresponding simulated images are shown in (c) and (d), respectively. Df-defocus, Th-thickness.

Figure 2. (a) Structural model for BNN. (b) The corresponding calculated images for defocus value -25 nm and specimen thickness 20 nm. Sites marked Na* and Na have different intensity despite same occupancy. (c) Experimental HAADF-STEM image of BNN. (d) Processed experimental image of BNN.