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Quantifying Oxygen Content in a Boron Rich Material by HAADF Way

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High angle annular dark field microscopy (HAADF) is a well known analytical technique especially suited for imaging heavy elements because the Z dependence of the electron scattering cross section involved. For the reason of small cross-sections, HAADF imaging of light atoms is very challenging. However, the situation has recently being improved with the development of Cs corrected electron microscope. This resulted in much sharper focus of the scanning electrons probe with more beam current within because of the large coherent convergence angle possible. In this presentation, we will show that one can successfully obtain HAADF imaging of atoms as light as boron in a boron rich material. Moreover, we will show that the efficiency of the HAADF technique means that quantitative determination of oxygen stoichiometry in a boron suboxide is feasible with higher spatial resolution than is possible using electron energy loss spectroscopy (EELS).

Figure 1 shows the atomic structure of the unit cell in a boron suboxide. Like many other boron-rich materials, it is a deformed close packed structure of boron icosahedral clusters occupying the vertices of a rhombohedral unit cell, with oxygen partially occupying the interstitutial sites marked red. Structurally, it may be considered as a close analogy of the fcc fullerine solids. However, as boron is electron deficient for covalent bonding, strong bonding exists between icosehedral units, resulting in a strongly linked covalent network. Thus boron rich materials are some of the strongest materials we know [1].

Fig. 1(a) shows the HAADF image of the boron suboxide in the [1-10] projection obtained using a VG601 scanning transmission electron microscope with a Nion Cs corrector. [2]. An advantage of HAADF imaging is the lack of image contrast reversal with sample thickness and relative simple image contrast interpretation. For example, we can directly recognize the boron icosahedral units by overlay the image with the schematic diagram (Fig. 1). At the current resolution (<0.145nm), we can partially identify the internal structure of the boron cluster, such as the ‘well-separated’ boron column, but not the closely packed atomic columns of boron and oxygen (Fig. 1b). A consequence of the small scattering cross section of light atoms is that high quality HAADF images are obtained in relatively thick sample of 80 nm.

Multislice image simulation has been carried out to understand quantitatively the image contrast. We can show that complex dynamical scattering effect are significant, but it is mostly confined to electron beam travelling down the closely spaced atomic columns not resolved in our imaging system. However, this does not prevent us from detecting a simple correlation between the relative image contrast of the boron clusters and the oxygen stoichiometry in the crystals, as shown in Fig. 2b-2d. We have used this to determine the local oxygen stoichiometry in this boron-rich materials to be $B_6O_{0.78}$, by matching the simulation with the experimental result (fig. 2 right panel). The result is consistent with that obtained from EELS which can not be pushed to atomic resolution because of the radiation damage limitation. The reason for the success of the quantitative relative HAADF image constrast analysis developed here will be discussed. We have applied the simulation to other materials or to the analysis of defects.

References
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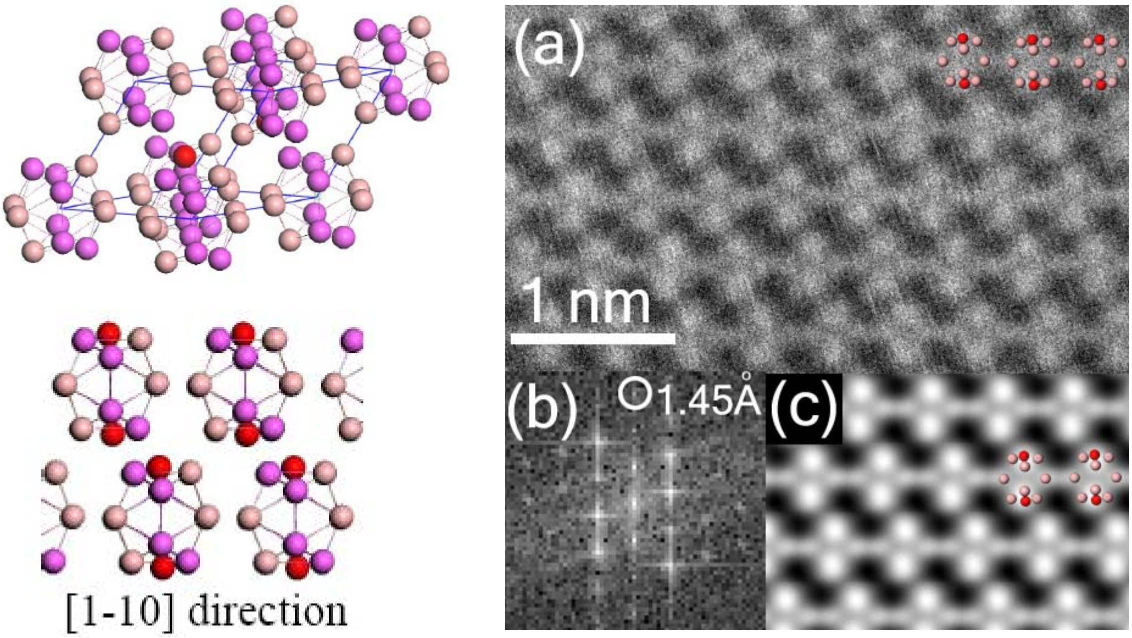

Fig. 1 The unit cell of the boron suboxide (top left) and the images of the boron cluster in [1-10] projection (bottom left). The right panel shows the experimental HAADF image of the boron suboxide also in [1-10] projection (a) with the corresponding power spectrum of the Fourier transform of the image (b) and the Fourier averaged reconstruction of the cluster image.

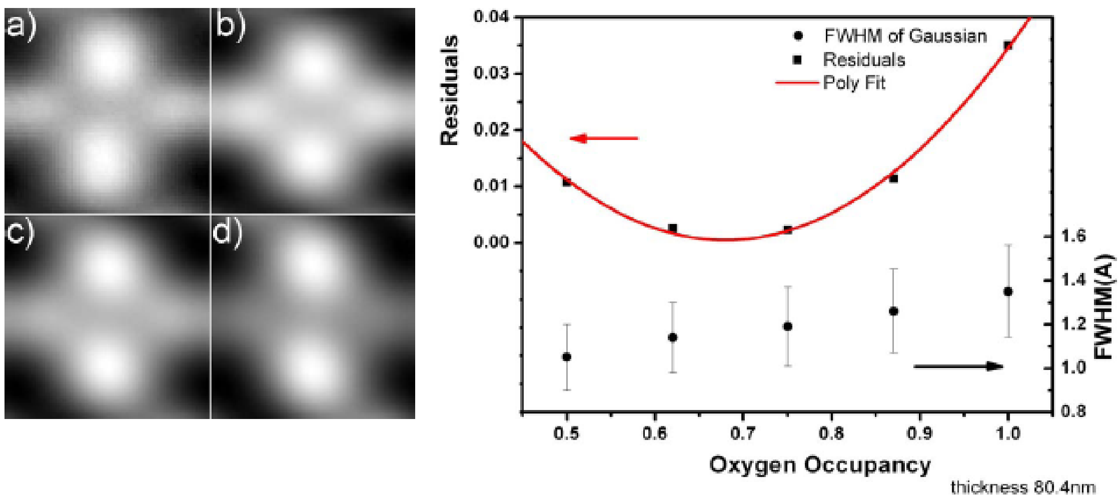

Fig. 2 (Left panel) The HAADF image of the boron cluster in boron suboxide (a) experimental image, (b)-(d) the simulation assuming oxygen content of 50%, 75% and 100% respectively. (Right panel). The dependence of residual between the relative contrast in the experimental image and that of the simulation, as a function of the proposed oxygen occupancy in the allowed interstitial sites. The minimum is taken to be the approximate oxygen stoichiometry in the imaged region. Also shown is the width of the Gaussian function used to broadening the simulation to be consistent with the experimental data. It does not depend sensitively with the proposed oxygen occupancy.