

# Experimental approach for the $\alpha$ exponent in $Z^\alpha$ by HAADF-STEM analysis: A binary approximation on $\text{Nb}_{16}\text{W}_{18}\text{O}_{94}$ ternary system.

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It is well known the fact that the concept of critical grain-size in materials induces changes on their physical properties. For example, the critical grain size is associated with the formation of multiple domain boundaries as a mechanism of additional strain relaxation in the grain [1]. In materials science, we must be able to determinate the domains occurrence, because these can produce quantum effects in the material behavior.

High Angular annular dark field (HAADF) imaging in STEM mode is able to provide structural and chemical information at atomic resolution. By this technique we have chemical and spatial characterization of the structure. The efficiency of this technique can provide direct imaging of the cation lattice along several projections particularly in inorganic oxides.

We report the observation of atomic column-domains, produced by non-uniformity intercalation of W and Nb atoms along the [001] projection. An ultra thin sample of the complex oxide  $\text{Nb}_{16}\text{W}_{18}\text{O}_{94}$  was observed using a high-angle annular dark field detector. While HRTEM technique is efficient to determine bulk crystallinity and defect structures, HAADF technique is superior in determining surface inhomogeneities and defects in the stoichiometric composition even at atomic resolution because it is possible to determine the chemical specie of the atoms involved by Z-contrast imaging process. An empirical calculation was developed to quantify the number of W atomic sites in excess at a specific column using a binary approximation in the ternary system  $\text{Nb}_{16}\text{W}_{18}\text{O}_{94}$ . This theoretical calculation is based on the fact that the profile line intensity in a HAADF image strongly depends on  $Z^\alpha$ , where the  $\alpha$  coefficient is between 1.5 to 2 (named: Z-contrast) and this effect generates observable column domains in the HAADF image recorder. The study was developed along the [001] zone axis projection. Some atomic columns observed by STEM-HAADF technique showed an excess of W atoms, this effect is directly related to the intensity distribution in the image generated by the HAADF scintillation detector.

On the other hand, an oxidation process with the atmosphere can generate ordered domains which correspond to higher oxides, as we can observe in figure 1 b). A large scale order of  $\text{Nb}_{12}\text{O}_{29}$  monoclinic structure is observed and also a  $\text{W}_x\text{O}_y$  can be differentiated by the contrast variation. The aligned flowers between  $\text{Nb}_{12}\text{O}_{29}$  cells present higher intensities, this is an indication of W atoms are present in these structures. The characterization of these oxides is still under study.

In conclusion, a single HAADF image allows us to deduce fractional composition for each cation independently. If we are able to know the dispersion factor, the unit cell and the thickness of the sample, we can determinate by using HAADF contrast imaging the atomic proportion of each chemical specie in each column given us a real chemical atomic resolution.

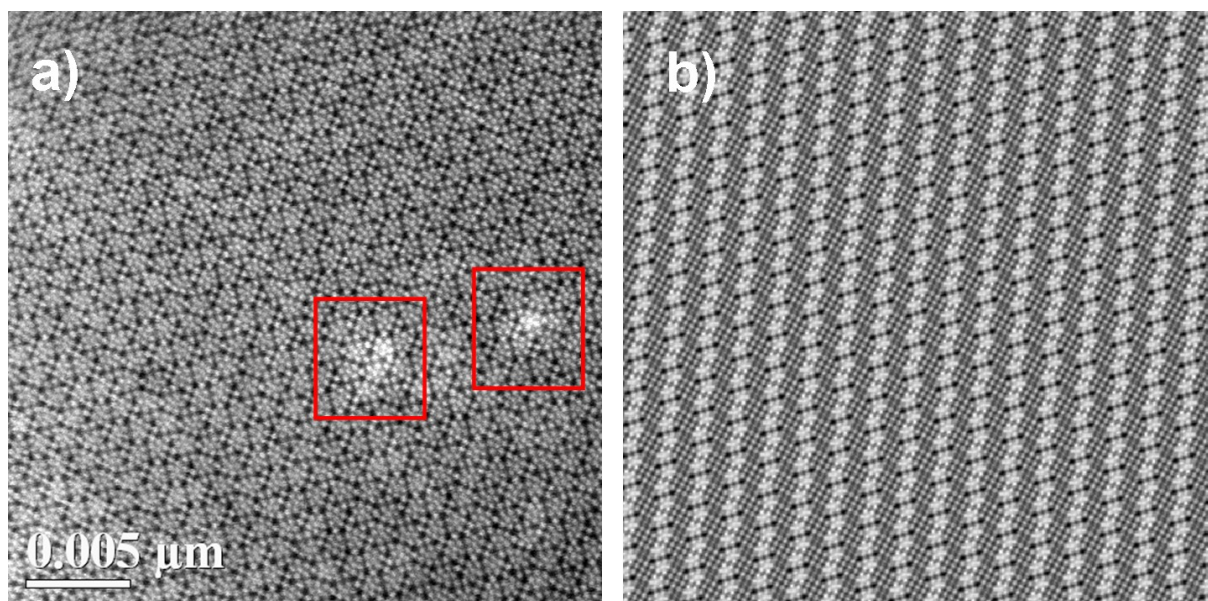


FIG. 1. a) HAADF image showing atomic column-domains in a single crystal Nb<sub>16</sub>W<sub>18</sub>O<sub>94</sub> octahedral structure. b) HAADF of ordered domains of Nb<sub>12</sub>O<sub>29</sub> (square structure) and a W<sub>x</sub>O<sub>y</sub> compound.

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