A valence selective x-ray fluorescence holography study of an yttrium oxide thin film - Supplementary information -

Abstract

In the main paper, we report on the first direct valence selective structure determination by x-ray fluorescence holography. The investigated sample consists of two layers (YO and Y_2O_3). The contributions of these layers are separated in order to obtain holograms of the 'pure' materials. This supplementary information gives an overview about the decomposition scheme for these holograms utilized in section 3.1. Secondly, in order to assess the reconstruction from single-energy holograms shown in the paper in section 4.1, we present the real space images of Y_2O_3 based on a reconstruction from 8 holograms.

1. Decomposition scheme

To decompose the individual contributions of the two sample layers (top: about 30 nm Y_2O_3 and bottom: 180 nm of YO), we assume that the holograms $\chi(\mathbf{k})$ measured at $E1$=17.041 keV and $E2$=17.054 keV are linear combinations of the holograms of pure YO and pure Y_2O_3.

$$\chi(\mathbf{k})_{E1} = a(\theta) \cdot \chi(\mathbf{k})_{\mathrm{YO}} + (1 - a(\theta)) \cdot \chi(\mathbf{k})_{\mathrm{Y_2O_3}} \tag{1}$$

$$\chi(\mathbf{k})_{E2} = b(\theta) \cdot \chi(\mathbf{k})_{\mathrm{YO}} + (1 - b(\theta)) \cdot \chi(\mathbf{k})_{\mathrm{Y_2O_3}} \tag{2}$$

with a and b denoting the relative contributions of the two compounds at the two energy values. These parameters depend on the polar angle θ due to the layered structure of the sample. The solution of this system of equations is (assuming that the 'pure' holograms of both materials are not affected by the small energy difference between E1 and E2):

$$\chi(\mathbf{k})_{\mathrm{YO}} = \frac{(1-b)\chi(\mathbf{k})_{E1} + (a-1) \cdot \chi(\mathbf{k})_{E2}}{a-b} \tag{3}$$

$$\chi(\mathbf{k})_{\mathrm{Y_2O_3}} = \frac{-b \cdot \chi(\mathbf{k})_{E1} + a \cdot \chi(\mathbf{k})_{E2}}{a-b} \tag{4}$$

The parameters a and b can be estimated from the ratio of the x-ray intensity absorbed in the two layers, i.e.

$$a, b \propto \frac{A_{\mathrm{YO}}}{A_{\mathrm{YO}} + A_{\mathrm{Y_2O_3}}} \tag{5}$$

with

$$A_{\mathrm{YO}} = T_{\mathrm{Y_2O_3}} \cdot (1 - T_{\mathrm{YO}}) \tag{6}$$

$$A_{\mathrm{Y_2O_3}} = 1 - T_{\mathrm{Y_2O_3}} \tag{7}$$

$$\tag{8}$$

with the Absorption coefficient A and the Transmission coefficient T defined as $T = e^{-\mu d/cos(\theta)}$, as usual.

2. Structure of Y_2O_3 and artifacts by the reconstruction from single-energy holograms

The reconstruction of the real space structure from a single hologram is subject to several problems, including the cancellation of real images and the occurrence of artificial signals. Computer simulations can help to assess the range of these effects by providing ideal holograms.

The simulations are based on a model structure of Y_2O_3 which is illustrated in Fig. h (Suppl.). The figure also indicates the xy lattice planes reconstructed from XFH with respect to the Y atoms in the corners of the unit cell. The structure of Y_2O_3 can be derived from the CaF_2 structure by removing one quarter of the anions and small displacements of the atoms. There are 32 Y atoms in the unit cell occupying two nonequivalent sites and only one type of O atom. The Y atoms are coordinated by 6 oxygens, while the oxygen is coordinated by 4 Y atoms.(Marezio, 1965)

We calculated theoretical holograms of Y_2O_3 for 8 energies between 17.5 and 21 keV with steps of 500 eV. These holograms were used to reconstruct the real space structure with a SPEA-L1 algorithm. The results are shown in Fig. h (Suppl.). It is observed that the real images are displaced from the idealized CaF_2 lattice (shown by the dashed lines), as indicated by the blue dashed ellipses. Only the signals at (5.3Å, 0Å) and (5.3Å, 5.3Å) in the (001) plane appear to be too close in each case and are not separated in the reconstruction. Several strong artificial signals (all signals not inside the dashed ellipses) are still observed, which are connected with the complex structure of Y_2O_3.

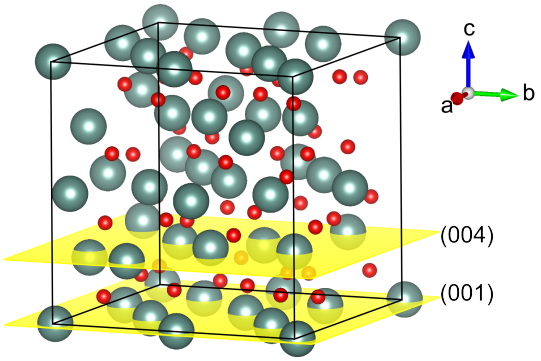

Fig. h. (Suppl.) Illustration of the crystal unit cell in Y_2O_3, indicating the xy planes reconstructed from XFH. (Note that different choices of the origin are possible in Y_2O_3.) Y atoms are colored blue, O red. Image was produced using VESTA (Momma & Izumi, 2011)

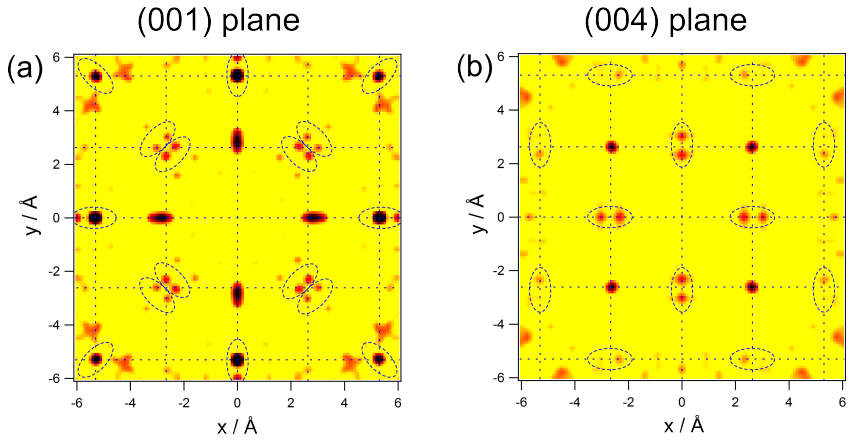

Fig. h. (Suppl.) Reconstruction of the (001) (a) and (004) (b) planes in Y_2O_3 from 8 simulated holograms with energies between 17.5 and 21 keV. The dashed ellipses mark the position of real images.

References

Momma K. & Izumi, F. (2011). J. Appl. Crystallogr. **44**, 1272.