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EXAFS of Nanocrystalline Y_2O_3

M. Winterer, R. Nitsche and H. Hahn

Thin Films Division, Materials Science Department, Technical University Darmstadt, Petersenstr. 23, 64287 Darmstadt, Germany

Abstract. A large volume fraction of atoms in nanocrystalline materials is located in surfaces and interfaces. Atoms facing the particle boundaries have a different local structure than atoms inside the particle. This heterogeneous disorder is investigated for nanocrystalline yttria powder by EXAFS spectroscopy.

1. INTRODUCTION

Nanocrystalline materials consist of grains with diameters of the order of 10 nm [1]. Therefore, a considerable amount of atoms is located in the volume formed by particle surfaces and interfaces. In principle, it is possible to investigate the heterogeneous disorder introduced by EXAFS spectroscopy. However, extracting the structural information from EXAFS data is difficult, because the EXAFS signal, $\chi(k)$, is amplitude-, $P(r) \cdot A(k)$, and phase-, $\Phi(k)$, modulated:

$$\chi(k) = \int_0^\infty P(r) \cdot A(k) \cdot \sin(2kr + \Phi(k)) dr \quad (1)$$

Here, we present for the first time results on a Zr-O model system and nanocrystalline Y_2O_3 powder with a mean particle size of 15 nm.

2. EXPERIMENTAL

Nanocrystalline Y_2O_3 powder was synthesized by inert gas condensation method through evaporation of Y metal with subsequent postoxidation [2]. The average particle sizes are estimated from TEM micrographs and BET measurements. Nanocrystalline powder of Y_2O_3 was dispersed in APIEZON grease for optimal thickness. XAFS spectra were measured at the Y-K edge at beamline X1.1 at HASYLAB/DESY. Samples were cooled in a liquid nitrogen bath cryostat to about 80 K. Measurements were performed in the QEXAFS mode [3] and up to 15 data sets were averaged.

3. DATA ANALYSIS

EXAFS data analysis was performed with the program xafs [4]. Three different methods are applied, a standard fit with coordination number N , distance R , Debye Waller factor σ^2 , and inner potential ΔE_0 as fit parameters, and a numerical distribution fit with σ^2 , ΔE_0 , and 25 bins (number of atoms at a certain distance) as fit parameters. A central peak and two symmetrical side peaks in the distribution histogram are degenerate for small deviations δ from $\alpha = 2kR$:

$$\sin(\alpha) \approx \frac{1}{2} (\sin(\alpha - \delta) + \sin(\alpha + \delta)) \quad (2)$$

We used the following procedure together with a reasonable bin width (here 0.04 Å) to remove this degeneracy. First, only 4 bins were fit at one time, starting with the lowest distance. A second fit is performed starting from the highest distance. Both histograms are averaged and a final fit is performed to refine the Debye Waller factor and inner potential until self consistency is obtained. Distribution reconstruction is performed by inverse sine fourier transform of reduced χ , where amplitude and phase modulations are removed using a feff standard. Structural parameters of the standard are fit to the data with a standard EXAFS fit (k^1 weighting). Splice points are chosen as small as possible [5]. EXAFS analysis was performed with feff [6] standards. An amplitude reduction factor of 0.9 was used.

4. RESULTS AND DISCUSSION

EXAFS was calculated for a model distribution using feff [6]. The model consisted of 8 oxygen atoms at the corners of a cube with a Zr atom in the center and distributed Zr-O distances (see vertical lines in bottom figure 1). This $\{\text{ZrO}_8\}$ cluster is used to establish the validity of the data analysis procedures. Results are summarized in table 1 together with neutron diffraction results for cubic Y_2O_3 at 77 K [7]. Radial distribution functions obtained and EXAFS fits are displayed in figures 1 and 2.

Table 1: Results of different EXAFS data analysis methods compared with neutron diffraction of cubic Y₂O₃.

{ZrO8} cluster					15 nm Y ₂ O ₃			cubic Y ₂ O ₃			
method ¹	model	s	h	d	s	h	d	s	h	d	nd, [7]
χ ² /N	8	5.3	8.1	7.7	4.3	5.3	5.0	6.5	6.4	6.5	6
<R>	2.32	2.25	2.32	2.31	2.25	2.30	2.24	2.28	2.27	2.25	2.285
σ ² / 10 ⁻⁴ Å	50	51	50	-	78	19	-	58	43	-	41
ΔE ₀	-	-2.3	0	-	1.0	2.8	-	3.8	2.8	-	-

¹EXAFS analysis methods: s: standard, n: numerical distribution fit, d: distribution reconstruction; nd: neutron diffraction

Figure 1: Results of EXAFS analysis for a model distribution. Top: simulated data (squares), standard EXAFS fit (wide grey line), and numerical distribution EXAFS fit (narrow black line). Bottom: radial distribution functions and integral distributions (smooth lines: reconstructed, steps: numerical distributions, vertical lines: model).

Figure 2: Results of EXAFS analysis of 15 nm Y₂O₃. Top: simulated data (squares), standard EXAFS fit (wide grey line), and numerical distribution EXAFS fit (narrow black line). Bottom: radial distribution functions and integral distributions (smooth lines: reconstructed, steps: numerical distributions).

The numerical distribution fit for the model distribution is in excellent agreement with the simulated data and the results are identical to the model input. Only the number of atoms in the individual bins is slightly too small, which can be explained by the limited band width of the back transformed EXAFS signal. Standard EXAFS analysis gives a coordination number artificially reduced by 34% and a distance reduced by 3%. The Y-O coordination in cubic Y₂O₃ has a narrow distribution and therefore, all three analysis methods give results with reasonable agreement with the neutron diffraction [7]. Nanocrystalline Y₂O₃ is fit best with the numerical distribution fit. Deviations from the data at higher k values are due to insufficient removal of low frequency noise. The oxygen coordination number is 5.3 but close to six within the error of the data analysis. The distribution function is broad and asymmetrical. Y-O distances at about 2.45 Å can be identified as Y-OH groups probably located at the particle surfaces. Similar Y-O distances are found in Y(OH)₃ [8].

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