EXAFS study of the local structure of crystalline and nanocrystalline $Y_2O_3$ using evolutionary algorithm method

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Abstract. Temperature-dependent local structure and lattice dynamics of yttria ($Y_2O_3$) were studied by X-ray absorption spectroscopy. Novel method, which combines the reverse Monte Carlo and evolutionary algorithm techniques, was applied for the analysis of extended X-ray absorption fine structure at the Y K-edge. This approach allowed us to reconstruct 3D atomic structure models of crystalline and nanocrystalline $Y_2O_3$.

1. Introduction
Yttria ($Y_2O_3$) is a material with a number of interesting technological applications, for instance, in the production of various ceramic materials and optical elements for rare-earth ion doped lasers [1]. Recently it was realized that addition of $Y_2O_3$ nanoparticles may significantly improve the high-temperature creep properties of steels [2, 3]. Such oxide dispersion-strengthened (ODS) steels are considered now as a promising structural materials for concentrated solar power plants and jet engines, and, in particular, for fusion and fission nuclear reactors [4].

Crystalline cubic $Y_2O_3$ has a body-centered cubic structure (space group $Ia3$) with the unit cell consisting of 80 atoms. Yttrium ions occupy two non-equivalent Wyckoff positions with different local environment [5] and different local symmetry: Y1 8(b) site with centrosymmetric $C_{3i}$ symmetry and Y2 24(d) site with noncentrosymmetric $C_2$ symmetry [6]. First-principles calculations of $Y_2O_3$ electronic properties [1] reveal slightly different Mulliken charges for two yttrium sites: $q(Y1) = +2.08$ and $q(Y2) = +2.10$.

Extended X-ray absorption fine structure (EXAFS) spectroscopy may be used to probe the local atomic structure of the material [7]. In this study we analyzed temperature-dependencies of the Y K-edge EXAFS for crystalline and nanocrystalline $Y_2O_3$ using a novel reverse Monte Carlo and evolutionary algorithm (RMC/EA) approach [8]. It allows us to study not only the first, but also further coordination shells around absorbing atom (yttrium), and to reconstruct a 3D-structure model of the material. We followed the evolution of this model upon temperature increase from 20 up to 1000$^\circ$C with the aim to analyze lattice dynamics of $Y_2O_3$ and, in particular, to investigate possible differences in the local environment of Y1 and Y2 ions. The results, obtained for crystalline $Y_2O_3$, are then compared with the ones, obtained for nanocrystalline $Y_2O_3$ with the particle size of about 50 nm.
2. Experimental and data analysis

X-ray absorption spectra of polycrystalline cubic \( Y_2O_3 \) (99.99%, Sigma-Aldrich) and nanocrystalline yttria (99.9%, size <50 nm (TEM), Sigma-Aldrich) were acquired at the Y K-edge (17038 eV) in transmission mode at the ELETTRA (Trieste, Italy) XAFS bending-magnet beamline [9]. The sample temperature was controlled in the range from 20 to 1000°C using the l’Aquila-Camerino vacuum glass furnace [9].

The experimental Y K-edge EXAFS spectra were extracted using the conventional procedure [10] and are shown together with their Fourier transforms (FT’s) in Fig. 1. The first peak in FT at \( \sim1.7 \) Å is due to the contribution of the first coordination shell (six closest oxygen atoms) around the absorbing yttrium atoms, whereas the second main peak at \( \sim3.2 \) Å corresponds mainly to the outer coordination shells, formed by yttrium atoms.

Experimental Y K-edge EXAFS spectra and their Fourier transforms for crystalline \( Y_2O_3 \) and nanocrystalline \( Y_2O_3 \) are compared in Fig. 2. As one can see, the amplitude of EXAFS spectrum and the height of all peaks in FT for nanocrystalline yttria is slightly reduced due to the additional static disorder.

3. RMC/EA simulations

Reverse Monte Carlo (RMC) method [11, 12] allows one to analyze EXAFS data taking into account the influence of multiple-scattering effects and contributions of outer coordination shells, as well as structural and thermal disorder. In this approach a 3D structure model is constructed and atomic coordinates are changed in an iterative random process, aimed to minimize the difference between experimental and configuration-averaged EXAFS spectra. The theoretical EXAFS spectrum is obtained by ab initio multiple-scattering calculation using the FEFF8 code [13] for the given structure model. Recently we have demonstrated that the implementation of the so-called evolutionary algorithm (EA) in the conventional RMC scheme significantly improves the convergence properties of the simulations and makes feasible the analysis of EXAFS spectra for complex materials [8, 14].

The RMC/EA-EXAFS analysis of crystalline and nanocrystalline yttria was performed at the Y K-edge. In both cases the material was modelled as an infinite crystal employing periodic boundary conditions for the supercell composed of \( 2\times2\times2 \) unit cells of cubic \( Y_2O_3 \) (Fig. 3). The value of the lattice parameter \( a_0 = 10.607 \) Å was fixed at the experimental value for crystalline
yttria obtained from neutron powder diffraction experiment [15].

In ab initio calculations of EXAFS spectra by the FEFF8 code [13] the multiple-scattering contributions were accounted up to the 4th order. Since yttrium ions occupy in Y2O3 two non-equivalent positions, the Y K-edge EXAFS spectra were calculated at each temperature for Y1 and Y2 sites separately, and the averaged EXAFS spectrum was calculated with the weights of 0.25 and 0.75 that correspond to the ratio of Y1 and Y2 atoms in Y2O3 structure. The averaged EXAFS spectrum then was used for the comparison with the experimental data.

The comparison of experimental and theoretical Y K-edge EXAFS spectra at each iteration was performed using Morlet wavelet transform (WT) [16, 17, 18] in the k-space range from 3.5 to 14.5 Å⁻¹ and in the R-space range from 1.0 to 6.9 Å. Thus we were able to account for the features of EXAFS spectra in k and R spaces simultaneously.

Good agreement between theoretical and experimental EXAFS spectra was obtained after 1500 iterations (Fig. 3). The final structural model was used to estimate the values of required structure parameters.

4. Local structure of crystalline Y2O3

Two non-equivalent Y sites in cubic yttria are schematically shown in the inset in Fig. 4. Each of Y ions is surrounded by six oxygen atoms, located at the vertices of slightly distorted cubes. For Y1 ions, located at centrosymmetric site, two unoccupied cube vertices correspond to the ends of body diagonal and at equilibrium all six Y1–O distances are equal. For Y2 ions, located at noncentrosymmetric site, two unoccupied cube vertices correspond to the ends of face diagonal, and three groups of Y2–O distances are slightly different [5].

The atomic radial distribution functions (RDFs) for Y–O and Y–Y pairs around both Y1 and Y2 can be calculated straightforwardly from the structure model, obtained in RMC/EA-EXAFS simulations (Fig. 4). Note that the nearest peaks of RDFs around Y1 and Y2 have close shapes and positions, whereas the distribution of atoms in outer coordination shells differs significantly.

The width of RDF peaks can be characterized using mean-square relative displacement (MSRD) factors σ². Temperature dependencies of the MSRD factors for yttrium–oxygen (Y–O) and yttrium–yttrium (Y1–Y2, Y2–Y2) bonds are compared in Fig. 5. To estimate the uncertainties of obtained results, RMC/EA-EXAFS calculations were repeated several times.
with different sequences of pseudo-random numbers [8]. Within such uncertainties, the obtained
MSRDs for all four non-equivalent Y–O bonds (one Y1–O and three Y2–O) have close values.
Temperature-dependencies of MSRDs for Y1–Y2 and Y2–Y2 atom pairs are, in turn, quite
different, although corresponding Y1–Y2 and Y2–Y2 distances are close: our results suggest
that the MSRD for Y2–Y2 pair is smaller and increases slowly when the temperature rises,
indicating that the atoms of Y2–Y2 pair interact strongly.

Temperature-dependencies of the MSRDs were best fitted using correlated Einstein model
[19]. Using the values of Einstein frequency $\omega_E$ one can estimate effective bond-strength
constants $\kappa = \frac{\omega_E^2}{\mu}$, where $\mu$ is reduced mass of corresponding atomic pair. The obtained
value for Y–O bond $\kappa = (100 \pm 4)$ N/m is in a good agreement with the value of bond-stretching
constant for Y–O bond, determined by infra-red and Raman spectroscopies (103 N/m in [20]
and 108 N/m in [21]).

The obtained effective bond-strength constants for Y–Y pairs are close to the value found
for Y–O pair: $\kappa = (115 \pm 1)$ N/m for Y2–Y2 pair and is about 25% larger than the effective
bond-strength constant $\kappa = (93 \pm 1)$ N/m for Y1–Y2 pair.

5. Local structure of nanocrystalline $Y_2O_3$
Reconstructed RDFs around Y atoms in nanocrystalline and crystalline $Y_2O_3$ are compared in
Fig. 6. The peaks of RDFs for nanocrystalline sample are slightly broadened with respect to those
for crystalline material. The MSRD values for Y–O, Y1–Y2 and Y2–Y2 pairs in nanocrystalline
$Y_2O_3$ are equal to (0.0059 $\pm$ 0.0006), (0.0057 $\pm$ 0.0002), (0.0047 $\pm$ 0.0003) Å$^2$, respectively, and
are close to corresponding values for crystalline sample at room temperature ((0.0049 $\pm$ 0.0005),
(0.0056 $\pm$ 0.0005), (0.0036 $\pm$ 0.0004) Å$^2$, respectively). Note that the MSRD value for Y–O bond
in nano-$Y_2O_3$ is close to that ((0.0059 $\pm$ 0.0016) Å$^2$), obtained in EXAFS studies of 40 nm $Y_2O_3$
particles doped with europium ions in [22]. One can conclude therefore that the size-related
effects are not pronounced for our nanocrystalline yttria sample.

6. Conclusions
The analysis of temperature-dependent Y K-edge EXAFS spectra of crystalline and
nanocrystalline $Y_2O_3$ has been performed using RMC/EA-EXAFS approach. This method
allowed us to obtain and investigate in details a 3D structure model of Y$_2$O$_3$ and to follow its evolution upon temperature increase. It was shown that there are no distinguishable differences in dynamics of Y–O bonds for both centrosymmetric Y1 and noncentrosymmetric Y2 sites. Nevertheless, such differences were observed for Y–Y atom pairs: it was shown that the interaction between neighboring Y2 atoms is stiffer than the interaction between neighboring Y2 and Y1 atoms. The results, obtained for nanocrystalline yttria with particle size below 50 nm, showed only minor increase in structural disorder with respect to microcrystalline material, and no significant size-related effects were observed.

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