Atomic structure and composition of the yttria-stabilized zirconia (111) surface

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Anomalous and nonanomalous surface X-ray diffraction is used to investigate the atomic structure and composition of the yttria-stabilized zirconia (YSZ)(111) surface. By simulation it is shown that the method is sensitive to Y surface segregation, but that the data must contain high enough Fourier components in order to distinguish between different models describing Y/Zr disorder. Data were collected at room temperature after two different annealing procedures. First by applying oxidative conditions at 10−5 mbar O2 and 700 K to the as-received samples, where we find that about 30% of the surface is covered by oxide islands, which are depleted in Y as compared with the bulk. After annealing in ultra-high vacuum at 1270 K the island morphology of the surface remains unchanged but the islands and the first near surface layer get significantly enriched in Y. Furthermore, the observation of Zr and oxygen vacancies implies the formation of a porous surface region. Our findings have important implications for the use of YSZ as solid oxide fuel cell electrode material where yttrium atoms and zirconium vacancies can act as reactive centers, as well as for the use of YSZ as substrate material for thin film and nanoparticle growth where defects control the nucleation process.

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1. Introduction

Atomic structure, composition and characteristic defects of yttria-stabilized zirconia (YSZ) surfaces are key to a basic understanding of this application relevant material. YSZ is for example frequently used in solid oxide fuel cells (SOFCs), which are regarded as a very promising technology to generate in a clean way electricity by direct conversion from chemical energy [1]. In such SOFCs, YSZ acts as solid electrolyte for oxygen ions and the surface and its interface with the electrode material play a central role in the relevant reactions: it is involved in the adsorption and oxidation of hydrocarbons, the formation of H2O and the oxidation of carbon monoxide at the anode as well as the dissociation and incorporation of oxygen at the cathode surface [1,2]. Hence, knowledge of the atomic structure and composition of YSZ surfaces and in particular characteristic defects is indispensable for a basic understanding of solid oxide fuel cell performance. Furthermore, details of the YSZ(111) atomic surface structure are crucial for an atomistic description of thin film and nanoparticle growth, for which YSZ is frequently used as substrate material [3].

The mostly used composition of YSZ contains 9.5 mol% yttria, which stabilizes the cubic phase of zirconia (C-YSZ) [4]. Density functional theory (DFT) calculations on low index C-YSZ surfaces predict that the non-polar, oxygen terminated (111) surface is the most stable one [5]. Despite its technological importance, experimental investigations of the C-YSZ(111) surface are scarce. Only recently it was observed by scanning tunneling microscopy (STM) at elevated temperatures that this surface exhibits a high number of defects [6], which are known to be important for surface reactions. Furthermore, at typical operation temperatures above 1000 K, a variation of the Y to Zr ratio is reported to change the performance of fuel cell devices considerably [7]. Contradictory results on Y and Zr surface segregation are reported, making a reconsideration of related chemical potentials necessary [6,8–10].

Here we present a combined anomalous and nonanomalous surface X-ray diffraction (SXRD) study to resolve the atomic structure and composition of the (111) surface of a 9.5 mol% yttria doped ZrO2 single crystal. Anomalous SXRD allows an X-ray scattering contrast variation between Zr and Y, which is essential for an element specific study of surface segregation [25]. To elucidate the role of the chemical environment on the surface structure and composition we employed two different sample treatments which are close to the conditions at the fuel cell cathode and the anode, respectively: A) heating the as-received sample at 700 K for 120 min at an oxygen pressure of 10−5 mbar (more oxidative), B) heating the sample to 1270 K for 145 min under ultra-high vacuum (UHV) conditions (more reductive). After these treatments the samples were quenched down to room temperature and it is to be expected that already segregated species remain in the near surface region.

Accompanying the data analysis we present surface structure factor calculations based on a statistical fluorite model for the YSZ

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bulk structure and the so-called Zr-shift model which is a more elaborate description based on the occupation of high symmetry sites by Y atoms and specific displacements of the surrounding Zr and O atoms. Although the final fits do not make use of the Zr-shift model, it is included here to show the sensitivity of the used technique and as a basis for future work.

2. Experimental details

Commercially available, wet-chemically polished YSZ single crystals with a miscut <0.1° were used. The experiments were carried out in a portable UHV chamber equipped with gas inlet and an electron bombardment sample heating. Prior to the synchrotron experiments, the preparation conditions for a chemically clean surface were established in a laboratory UHV system. Auger electron spectroscopy after treatment A showed that the sample surface was contamination free.

SRXD experiments were performed measuring crystal truncation rods (CTR) [11] at room temperature under UHV conditions at the Swiss Light Source (SLS) [12] and at the Angström-Quelle Karlsruhe (ANKA) [13]. At the SLS, both anomalous and nonanomalous data were recorded. Anomalous SRXD was performed on the same sample at the Y (17.038 keV) and Zr K-edges (17.998 keV). Nonanomalous data were collected at a photon energy of 16 keV (SLS) and at 10 keV on a second sample at ANKA. For both experiments the incident angle was fixed near the critical angle for total external reflection to improve the signal to noise ratio. From the obtained SRXD data it can be concluded that the sample preparation is very reproducible.

Data integration and merging of symmetry equivalents were performed using standard procedures [14,15]. Table 2 gives a summary of the data collection and subsequent merging results. Structure refinement was carried out using the ANA-ROD package [14] including the option to fit anomalous CTR data [16]. All the data measured at different X-ray energies are used at once to refine one structural model. In this way the composition of Y and Zr atoms can be refined to much higher accuracy.

The hexagonal surface unit cell has axes \(a_s, b_s, \) and \(c_s\) with \(a_s = b_s = \frac{3}{2}a, c_s = \sqrt{3}a\), whereby \(a\) is the parameter of the primitive cubic unit cell. The experiment gives the following surface cell parameters: \(a_s = b_s = 3.638 \AA, c_s = 8.912 \AA, \alpha = \beta = 90°, \) and \(\gamma = 120°\) from which we obtain that for our sample \(a_0 = 5.145(6) \AA\). By making use of an empirical linear relationship between cell parameters and yttria doping level \(a_0|A| = 5.1063 + 0.200x\) [17], we find \(x = 0.19\), with the composition \((1-x)\)ZrO\(_2\) · \(x\)YO\(_1.5\) (= Y\(_2\)Zr\(_1-x\)O\(_{2-x/2}\)). This is in good agreement with the supplier’s specifications (Cryotec Y1.72Zr0.086O1.913).

3. Bulk structure of YSZ and its (111) face

The idealized structure of cubic yttria-stabilized zirconia is of CaF\(_2\) type, with space group Fm \(_{3}\) m, see Fig. 1(a). Here, the Y and Zr atoms randomly occupy fcc (4a) sites, while the oxygens reside at interstitial (8c) \(\{\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\}\) -type positions [26]. However, many neutron and X-ray diffraction studies conclude to distortions from the ideal positions (see e.g. [18] and references therein). Although a controversial topic for some time, consensus has been found with a description of the structure where the anions displace along the \(\langle 110 \rangle\) and the cations along \(\langle 111 \rangle\) and cubic symmetry-related directions [19,20].

\[ f(Q, E) = f_0(Q) + f_\delta(E) + if'(E) \]

whereby \(Q\) is the momentum transfer \((|Q| = 4\sin(\theta)/\lambda, \) with \(\theta\) half the scattering angle and \(\lambda\) the wavelength), \(E\) the X-ray energy, \(f_0\) the atomic scattering factor far away of resonances, \(f'_\delta\) the dispersion correction and \(f'\) the absorption correction. Values of \(f'\) and \(f'_\delta\) used in the present study are taken from the NIST database [21] and listed in Table 1.

By making use of the corrected atomic scattering factors (Eq. (1)) it is straightforward to compute CTRs [16]. Fig. 3 shows simulated

| Energy (keV) | \(f_\gamma\) | \(f'_\gamma\) | \(f_\delta\) | \(f'_\delta\) |
|-------------|-------------|-------------|-------------|-------------|
| 10.0000     | 0.00        | 0.00        | 0.00        | 0.00        |
| 16.0000     | -2.80       | 0.50        | -1.50       | 0.60        |
| 17.0384     | -5.85       | 1.02        | -2.44       | 0.57        |
| 17.8876     | -2.01       | 3.38        | -5.79       | 1.05        |

4. Results

4.1. Anomalous dispersion and simulations

In this section the scattering along CTRs of the YSZ(111) surface is discussed for both the fluorite as well as the Zr-shift models. In order to distinguish between the scattering contributions of Y and Zr, it is needed to exploit the anomalous diffraction effect due to element specific X-ray-induced electronic transitions. Whereas the atomic scattering factors of Y (Z = 39) and Zr (Z = 40) far away from resonances (\(f_0\)) are almost identical, the X-ray absorption behavior is different. The scattering of a particular element near its absorption edge alters for which the following corrections are made to the atomic scattering factor \(f\):

\[ f(Q, E) = f_0(Q) + f_\delta(E) + if'(E) \]

| Energy (keV) | \(R_{\text{merge}} \) | \(R_{\text{merge}} \) | \(R_{\text{merge}} \) | \(R_{\text{merge}} \) |
|-------------|----------------------|----------------------|----------------------|----------------------|
| 10.0000     | 373                  | 0.14                  | 239                  | 0.053                |
| 16.0000     | 431                  | 0.096                 | 370                  | 0.082                |
| 17.0384     | 371                  | 0.154                 | 421                  | 0.119                |
| 17.8876     | 0.86                 | 1.03                  | 1.40                 | 0.09                 |

Table 2 Data reduction and refinement results. The agreement of merging symmetry equivalent data points is given by \(R_{\text{merge}} = \frac{\sum_{i=1}^{N} \left| F_{\text{obs},i} - F_{\text{calc},i} \right|}{\sum_{i=1}^{N} \left| F_{\text{calc},i} \right|}.\) At the bottom are listed the residuals for the best fits. These are defined as \(R^{2} = \sum_{i=1}^{N} \left( \frac{f_{\text{obs},i} - f_{\text{calc},i}}{f_{\text{obs},i}} \right)^2.\)
CTR s for Y-rich and bulk terminated YSZ(111) surfaces, calculated at the Y K-edge (anomalous) and far from any resonances (nonanomalous). The simulations serve to show the expected differences between the Zr-shift and fluorite models and the sensitivity towards Y-segregation when using anomalous diffraction. Two different surface compositions are shown: one with a top layer consisting of 100\% of pure Y and the other with Y_{0.174}Zr_{0.826}, the composition as in the bulk of the crystal. All simulations are carried out assuming bulklike atomic positions (see Table 6) and oxygen termination (see Fig. 2). The Debye–Waller parameters of the top layer, which consists of oxygen–metal–oxygen, are chosen as those for the fluorite structure (Table 6). In this way it is investigated what the difference in expected diffracted intensity due to a different bulk model but with the same surface structure will be.

Whereas the CTRs at relatively low momentum transfer for the different situations are close together, those at high momentum transfer become clearly distinguishable. In particular, the differences between nonanomalous and anomalous CTRs for the Zr-shift model are clearly different at high momentum transfer. At low momentum transfer, the Zr-shift and fluorite models give basically the same CTRs. This is understood from the fact that the displacements of the atoms in the Zr-shift model are relatively small (of the order 0.2 Å), which makes their influence on the scattered intensities apparent only at high enough momentum transfer. The same is also seen in the phase, $\phi$, of the total structure factor, which is basically the same for both models and only starts to differ for high $Q$ at the Y-edge. At relatively low values of $Q$, the intensities and phases of the Zr-shift model and the average fluorite structure including enhanced Debye–Waller parameters, which take into account some static disorder, are basically the same. Due to this similarity, in particular at low momentum transfer, between the scattered intensities for both models, the fluorite model (Fig. 2) is expected to give a very good description of the average structure.

For both structural models there is however a difference between the nonanomalous and Y-edge case. This is seen in the shape of the CTR signal in between the Bragg peaks: the structure factor of the Y-rich surface at the Y-edge is less rounded and more pointy. This is the typical shape one would expect when the surface contains less scattering strength than the bulk underneath, which is the case here. It is expected that when data are collected at three different X-ray energies (Y, Zr K-edges and nonanomalous) it will be possible to refine the surface composition, also when the differences are relatively small [16].

### 4.2. Refinement

Structural model refinement is carried out with a strategy exploiting as much information as possible, which is done by using all the data measured at different X-ray energies for one treatment at once. One structural model is refined against data sets which differ in their sensitivity towards the crystal’s chemical composition. In this way, correlations between various fit parameters, most notably the Y and Zr occupancies, are reduced to a large extent. In Table 2 an overview of the different data sets and the goodness of fit are given.

The different data sets are recorded in a $Q$-range which does not include high enough Fourier components to distinguish between the fluorite and Zr-shift models, as explained in the previous paragraph. Indeed, trying to refine parameters within the Zr-shift model did not lead to physically reasonable results, which is an indication that the data are not sensitive to the particular displacements within this model. The bulk crystallographic study of Ishizawa et al. [20] makes use of data sets with (cubic) $h$, $k$ and $l$ values up to 12, which are high enough to refine the particular atomic displacements. The surface sensitive data collections for the samples used here, gave measurable signal only up to $h$ and $k$ values of 2 and $l$ up to 8 (in the cubic system $h$, $k$, $l$ up to approximately 4). Therefore, we have used the fluorite model for structure refinement here. This model includes all the important parameters, such as surface composition and relaxation, needed for a
Fig. 3. Simulations for the (2,2) CTR up to the highest attainable L-value for an X-ray energy of approximately 17 keV. Shown are the modulus of the structure factor (|F|) calculated for the nonanomalous case (a) and at the Y K-edge (c) for the ideal fluorite (blue) model and the Zr-shift model (red). The case of Y segregation is investigated by assuming a bulk oxygen-terminated YSZ(111) surface of which the last metal layer is completely composed of Y versus a surface with a bulklike composition. Calculations of |F| for the two different surface compositions (dashed and solid lines) are displaced by a factor of 10 for clarity. (a) (2,2) CTR for a Y-segregated surface (solid) and a surface without preferential segregation (dashed) in the nonanomalous case. (b) The phases (ψ) of the structure factor for the Y-segregated surface as in a). (c) (2,2) CTR for a Y-segregated surface (solid) and a surface without preferential segregation (dashed) at the YK-edge. (d) The phases (ψ) of the structure factor for the Y-segregated surface as in (c). Clearly the differences between all the different models become more pronounced at high momentum transfer. At relatively low momentum transfer the ideal fluorite model and the Zr-shift model become indistinguishable, whereas the differences between the nonanomalous and Y K-edge cases are present for the entire Q-range.

The results of the refinement for sample 2 are listed in Table 3. CTR data and fits for sample 2 are shown in Figs. 4 and 5. For sample 1 only a nonanomalous data set was recorded, therefore, no information about the composition could be deduced for this sample, merely the morphology. For sample 2 also the composition is deduced from the fits. Table 5 lists the relative Y concentration, defined as the Y occupancy divided by the total site occupancy, in the islands and terminating layer.

The most striking feature of all data sets is that the measured intensity is much lower than what would be expected for bulk terminated crystals. This means that the electron density in the surface region is substantially reduced. The best fits obtained here indicate that the crystals are not terminated by a complete crystal layer, but rather a fraction of that which can be interpreted as the occurrence of islands on the surface with a size much smaller than the X-ray coherence length of the order of 5000–10000 Å. The layer beneath these islands actually represents the crystal’s terminating plane. Table 4 lists the (fractional) coverage of the islands found for samples 1 and 2 and both treatments. The island coverage is about 30% after the initial treatment under oxygen and it is slightly reduced after the high temperature treatment of sample 2. Also the crystal terminating plane is affected (see Table 3); the metal ion occupancy changes from 100% (treatment A) to 92% (treatment B), indicating a porous near surface region. This is further substantiated by calculating the total metal concentration in the islands and last crystal plane, which reduces significantly from 1.4(1) to 1.15(6) after the UHV anneal.

Concerning the relative Y/Zr concentrations, we observe the following trend from the fit of data set 2: after the initial oxygen cleaning treatment at 700 K, both the oxide islands and the crystal terminating plane are slightly understoichiometric in Y. After annealing to 1270 K under UHV conditions, the fit indicates an enrichment of Y at the surface with 89% relative Y occupancy in the islands and 30% in the crystal terminating plane. The metal ions in the islands undergo a slight inward displacement. This relaxation seems more pronounced for the Zr ions, but the fit is actually not very sensitive to this positional parameter because the occupancy has reduced to almost zero. The Debye–Waller

detailed understanding of the structure. The cationic and anionic disorder, known to be present in YSZ, is readily modeled by enlarged Debye–Waller parameters. The fluorite model is expected to be an adequate description of the X-ray scattering, in particular in the measured Q-range.

Table 3
Refined atomic coordinates for sample 2 after treatments A and B. Shown are the results for the fluorite model, of which the bulk atomic coordinates and occupancies are listed in Table 6. Values in brackets denote the estimated standard deviations (e.s.d.) obtained from the fitting procedure. Parameters that were fixed are listed without e.s.d.

| Atom | Treatment A | Treatment B | z | B | θ |
|------|-------------|-------------|---|---|---|
| O1   | 0.89(5)     | 0.760(4)    | 16(4) | 0(1) | 0.17(4) |
| Y1   | 0.67(5)     | 0.651(1)    | 0(2) | 0(2) | 0.21(2) |
| O2   | 0.333       | 0.333       | 2(1) | 2(1) | 0.28(4) |
| O3   | 0.415(3)    | 0.423(3)    | 2(1) | 2(1) | 0.73(9) |
| Y2   | 0.333       | 0.333       | 2(4) | 2(1) | 0.28(4) |
| O4   | 0.585(6)    | 0.569(5)    | 2(1) | 2(1) | 0.41(7) |
| O5   | 0.333       | 0.333       | 2(4) | 3.5(7) | 0.36(6) |
| Zr1  | 0.647(3)    | 0.551(1)    | 9(4) | 0.88(7) | 0.2(1) |
| Zr2  | 0.67(5)     | 0.651(1)    | 0(2) | 0.02(1) | 0.02(1) |
| Zr3  | 0.333       | 0.333       | 2(1) | 2.0(5) | 0.64(4) |
| Zr4  | 0.585(6)    | 0.569(5)    | 2(1) | 0.23(2) | 0.23(2) |
The STM measurements indicate the presence of islands about 0.2 nm in height, with static disorder. It is an interesting observation that the YSZ(111) surface exhibits smooth surfaces, characterized by large terraces, and small nanoparticles. The STM study shows that annealing in air is known to cause Y segregation. Here we find that annealing in vacuum also results in Y segregation. Comparison with the theoretical surface phase diagram of YSZ(111) [8] shows that the partial oxygen pressure must be as low as 10^{-30} mbar before the surface region becomes Zr-rich around 1200 K. We estimate from the total pressure during our annealing step (treatment B) of 10^{-8} – 10^{-9} mbar that the oxygen partial pressure is not better than 10^{-12} – 10^{-15} mbar and is therefore in agreement with the predicted segregation behavior.

As a consequence for the operation of SOFCs, the high surface Y concentration and related high oxygen vacancy density under more oxidative conditions will facilitate oxygen incorporation at the fuel cell cathode. However, since defects are also active sites for the H2O formation on the anode side, a lower Y concentration and the decreased number of defects under more reductive conditions can be considered as a limiting factor in the efficiency [24]. Tailoring the composition, structure and defect concentration at fuel cell electrode surfaces will therefore be a key issue to increase SOFC performance.

For the use of YSZ as a substrate material in thin film and nanoparticle growth, our results also have consequences. First of all, we have shown that commercially available polished substrates have a surface island morphology. Second, we demonstrated that the surface composition and defect concentration depends on the annealing conditions (oxygen pressure and temperature). Most thin film growth techniques are for a large part determined by kinetics, which depend heavily on surface defects. Such defects may also facilitate heterogeneous nucleation and strain relaxation. Tailoring of the surface vacancy density and composition by different annealing conditions can have a direct influence on the final film structure and properties. It is also to be expected that the exact surface defect structure will influence the distribution and size of nanoparticles grown on the surface; defects will limit the surface diffusion length thereby enabling the growth of more and smaller nanoparticles.

In summary, we derived an atomic structure model for the pristine (111) surface of c-ysz after oxidative and reductive treatments. The results obtained from (anomalous) surface X-ray diffraction are consistent with DFT calculations [8], STM measurements [22] and bulk X-ray diffraction [20]. Our results reveal an increased Y concentration at the surface and a high vacancy density, of both Zr and oxygen, in the topmost layer under both studied conditions. The heat treatment under reductive conditions leads to a higher ordering in the surface and an increase of the Y concentration. Our findings are of importance for obtaining fundamental knowledge and understanding of the growth of thin films and nanoparticles on this surface and they set the basis for the

| Layer          | Treatment A | Treatment B | Bulk   |
|---------------|-------------|-------------|--------|
|               | \(N_e\)     | \(N_i\)     | \(N_r\) |
| Last cryst.   | 0.14(6)     | 0.0(1)      | 0.30(3)|
| Islands       | 0.0(1)      | 0.63(8)     | 0.89(3)|

Table 5

Results of cation composition of the surface islands and last crystal layer of sample 2 for treatments A and B. Shown are values for \(N_e = N_c / (N_c + N_v)\) the relative Y occupancy (\(N_{\text{fl}} = 0.174\)) and □ the fractional amount of vacancies.

5. Discussion & conclusions

The results indicate the presence of islands on the surface and an increased vacancy density in the crystal terminating plane. Also, Scanning Tunneling Microscopy (STM) reveals a surface morphology containing islands [22], even after annealing to 1270 K at 1 bar oxygen pressure. Our STM measurements indicate the presence of islands about 0.2 nm high, 1 nm wide and with a lateral spacing of 1-2 nm, which results in a surface coverage in the 25-50% range. The island height as determined by STM might be somewhat too low, because of tip convolution effects. Our X-ray study reveals islands of about 0.3 nm height and a coverage of about 30%, completely in agreement with the STM study. It is important to note that the lateral spacing between the islands is too small for regular atomic force microscopy to be resolved, because of the poorer resolution. Indeed, our own AFM measurements (not shown here) show smooth surfaces, characterized by large terraces. Only the use of very sharp AFM tips would make it possible to resolve the island structure. It is an interesting observation that the YSZ(111) surface exhibits atomic roughness in the form of islands and vacancies over a wide O2 pressure (UVH to 1 bar) range up to high temperatures (1270 K), which lets us conclude that this may be an intrinsic property of this surface, not related to the initial sample polishing process. Annealing in air is known to cause Y segregation. Here we find that annealing in vacuum also results in Y segregation. Comparison with the theoretical surface phase diagram of YSZ(111) [8] shows that the partial oxygen pressure must be as low as 10^{-30} mbar before the surface region becomes Zr-rich around 1200 K. We estimate from the total pressure during our annealing step (treatment B) of 10^{-8} – 10^{-9} mbar that

\[
\begin{array}{cccccc}
\text{Atom} & \text{Fluorite} & \text{Zr-shift} \\
\hline
\text{O} & 1 & 1/3 & 2/3 & 11/12 & 2.3 & 0.9565 \\
\text{O} & 6 & 0 & 0 & 3/4 & 0.9565 \\
\text{O} & 6 & 0 & 2/3 & 0.174 & 0.9565 \\
\text{O} & 6 & 0 & 0 & 0.174 & 0.9565 \\
\text{Zr} & 1 & 1/3 & 2/3 & 2/3 & 0.174 & 0.9565 \\
\text{Zr} & 8 & 0 & 0 & 0 & 0.174 & 0.9565 \\
\text{Zr} & 8 & 0 & 2/3 & 2/3 & 0.174 & 0.9565 \\
\end{array}
\]

Table 6

Atom fractional coordinates in the (111)-oriented unit cells of the fluorite and Zr-shift models. Listed are the atoms, whereby those displaced in Zr-shift model are indicated by a prime, the Debye-Waller parameters (\(B\)), the site multiplicities (\(m\)), the site occupancies (\(\theta\)) and the displacements in the Zr-shift model (\(\Delta\)).
Fig. 4. CTR data and fits for treatment A of sample 2. Shown are different CTRs \((h,k)\) measured at the Y-edge (Y) and Zr-edge (Zr).
Fig. 5. CTR data and fits for treatment B of sample 2. Shown are different CTRs \((h,k)\) measured at a nonanomalous X-ray energy (N) and at the Y-edge (Y) and Zr-edges (Zr).
experiments aimed at the atomicistic understanding of SOFC electrodes under operational conditions, which is essential for SOFC implementation in our future energy balance.

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Appendix A. Transformation of atomic co-ordinates

Transformation between the cubic and the (111)-oriented unit cell used for our SXRD measurements is carried out by use of the following matrix:

\[
M = \begin{pmatrix}
1/2 & 0 & -1/2 \\
-1/2 & 1 & 1 \\
-1 & 1/2 & -1/2
\end{pmatrix}
\]

The cell axes are then written as \(a_{111} = Ma_{cub}\), with the index \(i = 1, 2, 3\) indicating the three different crystal axes. Using \(a_0\) as the cubic unit cell parameter, gives \(a_{111} = a_{cub} = \sqrt{3}a_0\). The fractional coordinates of the displaced atoms in the (111)-oriented cell model can be written in terms of the displacement \(\delta\) in the following way:

\[
\begin{pmatrix}
x + \delta_x \\
y + \delta_y \\
z + \delta_z
\end{pmatrix}_{111} = \begin{pmatrix}
x_{cub} \\
y_{cub} \\
z_{cub}
\end{pmatrix} + \begin{pmatrix}
\delta_x \\
\delta_y \\
\delta_z
\end{pmatrix}_{cub}
\]

These relate to the ideal fluorite positions \((x_0, y_0, z_0)\) as:

\[
\begin{pmatrix}
x_0 \\
y_0 \\
z_0
\end{pmatrix}_{111} = \begin{pmatrix}
x_{cub} \\
y_{cub} \\
z_{cub}
\end{pmatrix} + \begin{pmatrix}
\delta_x \\
\delta_y \\
\delta_z
\end{pmatrix}_{cub}
\]

Here, we will use the notation \(\Delta = \frac{1}{2}\delta\) to indicate the fractional amount of displacement from the ideal cubic position in the (111)-oriented surface unit cell. Zr atoms in the Zr-shift model then occupy positions displaced from the ideal \((x_0, y_0, z_0)\) positions by:

\[
\begin{aligned}
(0, 0, 3\Delta) & \quad (4\Delta, 4\Delta, \Delta) \\
(4\Delta, 4\Delta, \Delta) & \quad (8\Delta, 4\Delta, \Delta) \\
(4\Delta, 8\Delta, \Delta) & \quad (4\Delta, 8\Delta, \Delta) \\
(8\Delta, 4\Delta, \Delta) & \quad (0, 0, 3\Delta)
\end{aligned}
\]

And part of the oxygen atoms occupy positions displaced from their ideal positions given by:

\[
\begin{aligned}
(2\Delta, 2\Delta, \Delta) & \quad (2\Delta, 2\Delta, \Delta) \\
(2\Delta, 4\Delta, \Delta) & \quad (2\Delta, 4\Delta, \Delta) \\
(4\Delta, 2\Delta, \Delta) & \quad (4\Delta, 2\Delta, \Delta)
\end{aligned}
\]

Note that the symmetry of these displacements also involves the 3-fold inversion axis, i.e. \((x, y, z)\) equivalent to \((y, x, z)\), which is present in the fluorite structure. As an example of the relation between \(\delta\) and \(\Delta\) consider a Zr atom occupying a position displaced \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\) [27] from the Y atom sitting at the origin of the cubic unit cell. The ideal fluorite positions for both atoms \((x_0, y_0, z_0) = (0, 0, 0)\) are the same in the cubic and (111)-oriented unit cells. The fractional coordinates of this particular atom in the (111) oriented cell will be \((M^{-1})^T(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})\) (4\(\Delta, 8\Delta, \Delta\)). Table 6 lists the atomic positions, occupancies and Debye–Waller parameters used in the bulk models of the fluorite and Zr-shift models.

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[25] The atomic form factor of both elements is reduced by about 15% at the respective K edges.
[26] See International Tables for Crystallography, Vol. A: Space group symmetry, Kluwer Academic Publisher 1995.
[27] The displacement is given by \(\sqrt{3}a_0 = 0.19\AA\).