Detailed TEM characterization of PbTiO$_3$ nanorods

R Sæterli$^1$, ATJ van Helvoort$^1$, G Wang$^2$, PM Rørvik$^2$, BS Tanem$^3$, T Grande$^3$, M-A Einarsrud$^2$ and R Holmestad$^1$

1 Department of Physics, NTNU, N-7491 Trondheim, Norway
2 Department of Materials Science and Engineering, NTNU, N-7491 Trondheim, Norway
3 SINTEF Materials and Chemistry, N-7491 Trondheim, Norway

* Corresponding author: ragnhild.saterli@ntnu.no

Abstract. 1D functional oxides at nm-scale are interesting for fundamental reasons and promising for future applications. Here, ferroelectric PbTiO$_3$ nanorods, produced through a hydrothermal process, have been studied in detail by transmission electron microscopy. The length (up to one µm) and the diameter (30-100 nm) as well as the growth direction ([001]) of the nanorods could easily be determined using conventional imaging and electron diffraction techniques. However, variations along the length of the rods were clearly visible in the bright field images. Steps on the outer surfaces of the rods could be identified using energy filtered transmission electron microscopy and spectrum imaging thickness maps. The thickness variation parallel to the electron beam affected the bright field contrast and energy dispersive spectroscopy of the nanorods. From cross-sectional specimens, it was determined that the outer surfaces of the rods were dominantly {110} type, leading to a rectangular cross-section. The cross-section diameter of the rods was reduced by the introduction of {100} surfaces. In addition, the cross-sectioned specimen revealed the presence of internal channels in the growth direction, especially in the bottom part of the rods. Such a detailed structural description of the nanorods was necessary to study the possible ferroelectric domain structure and to reveal the growth mechanism of the rods.

1. Introduction

Ferroelectric materials such as the tetragonal perovskite lead titanate (PbTiO$_3$, unit cell parameters $a = b = 3.90$ Å and $c = 4.15$ Å) are highly interesting to the electronics industry in for example non-volatile memory devices. The ferroelectricity of PbTiO$_3$ arises due to an overlap of the lead and oxygen shells, resulting in a net polarization along the $c$ ([001]) direction. In order to implement PbTiO$_3$ and similar materials into devices, an understanding of the properties of the materials at the nanoscale is vital. It is for example well known, although not completely understood, that PbTiO$_3$ becomes less ferroelectric and less tetragonal as the size of the material decreases. The introduction of reduced dimensionality such as in thin films or nanorods may therefore affect the ferroelectric properties of the material. At the nanometer scale, surface and internal defects may also alter the ferroelectricity by introducing screening charges and pinning centers for domain walls. Hence, the understanding of the connection between size, dimensionality, structure and ferroelectricity is important for the use of the material in future applications.
2. Experimental details

PbTiO₃ specimens were prepared through a relatively simple hydrothermal synthesis route using Pb-Ti-citrate sol as precursor and the surfactant sodium dodecylbenzene sulfonate (SDBS). More details on the synthesis can be found elsewhere [1,2]. The resulting powder products were prepared for transmission electron microscopy (TEM) studies by two different sample preparation methods. Some of the powder was dispersed in ethanol and ultrasonically dispersed in order to separate the rods. The ethanol with the powder was then dripped on to a holey carbon grid before left to dry, resulting in a side-view of the nanorods as they land flat on the carbon film. The second technique was to embed the powder in epoxy before microtoming to slices of a thickness of approximately 50 nm, measured by the ratio of inelastic to elastic scattering by the use of electron energy-loss spectrometry (EELS). This second sample preparation technique resulted in a cross-section view of the rods.

The specimens were studied in a Philips CM30 and a JEOL2010F microscope, both operated at 200 kV. The CM30 was used for bright field (BF) and dark field (DF) imaging as well as selected area electron diffraction (SAED). The 2010F was fitted with a GIF2000 spectrometer for energy filtered imaging (EFTEM) and spectrum imaging (SI) thickness mapping, and was in addition used for high resolution electron microscopy (HREM) and energy dispersive x-ray spectroscopy (EDS, Oxford INCA).

3. Results

The powder sample consisted of microspheres with rods pointing out from the surface, as seen in figure 1a. Both microspheres and rods were found by EDS and SAED to be pure tetragonal PbTiO₃.

The growth direction of the nanorods was determined by HREM imaging and SAED of the side-view specimen to be the c direction, parallel to the polarization direction. HREM and SAED results of a typical rod are shown in figure 1. The diameters of the rods varied between 30 and 100 nm, with a decrease in diameter towards the end furthest away from the microsphere. The rods were up to one micrometer long.

Figure 1: (a) BF image of microsphere. (b) BF image of rod with (c) HREM image of the tip and (d) SAED pattern showing a growth direction of [001].

The outer surfaces of the rods were determined through HREM imaging of the cross-section specimen, as shown in figure 2 after tilting to the [001] orientation. Figures 2a-c show typical cross-sections, revealing that the surfaces are situated dominantly on {110} planes. {100} planes are the second most common surface planes, often seen to cut the corners of the {110} surfaces, as pointed out with black arrows in figure 2b. Examples were found where the surfaces were not situated along any major crystallographic planes, one of which is given in figure 2d. The cross-sections of the rods showed that a majority of the rods contain tunnels that extend through the thickness of the cross-section specimen, in the c direction of the rods. These internal defects seem to outline building blocks of approximately 10 by 10 nm which the rods were composed of. This is clearly visible in the cross-section depicted in figure 2c. These building blocks aligned and assembled perfectly in the c direction of the rods, while they were in several cases found to grow together with a small mismatch (less than one degree) in the lattice directions perpendicular to the growth direction. Cross-sections with
rectangular outer surfaces had in general less internal defects such as tunnels and rotational mismatch between building blocks than irregular shaped cross-sections.

As the specimen was cut at arbitrary places along the rods during cross-section sample preparation, EFTEM thickness mapping and SI line scans at different positions along the rods were used to determine the shape evolution from the thinner end (tip) to the end connected to the microsphere (bottom) end of the rods. It was found that the shape of the rods was more regular at the tip, while the bottom usually has a more irregular cross-section shape. The shape development of one rod is shown in figure 3. The thickness plots in figure 3b may indicate that the rod was square at the tip, while the bottom had a more complex shape. The difference between the two lower graphs may be interpreted as due to the introduction of {100} surfaces.

Figure 4 shows the BF image and EDS line scan measurements on a rod with a tunnel, illustrating how the BF contrast and intensity of the EDS signal varied with the cross-section shape of the rod.

In order to examine the possible 180° domain structure of the rods by TEM, a series of dark field experiments, as described in reference [4], were performed, in which no clear domain structure could be revealed.
The tunnels and holes in the c direction arose as the building blocks grew together with a small rotation mismatch or due to deviations from a perfectly rectangular shape. These deviations became fewer toward the tip of the rods, which could be ascribed to a ripening of these building blocks before they were attached to the rod.

The reason for the inconclusive DF experiments was the irregular shape of the rods, with the varying thickness and surface steps as well as the tunnels and rotation of building blocks all gave unwanted diffraction and thickness contrast which masked any contrast from 180° domains. A further complication arose as domains were visible only when viewed edge-on, that is, when the wall is parallel to the electron beam. In addition, the ferroelectricity and domain structure itself could be expected to vary from needle to needle due to domain wall pinning to the tunnels and the internal defects possibly creating screening charges. Further domain structure experiments are in progress and will be performed on more homogeneous rods.

The two sample preparation methods used in this study combined gave a full 3D picture of the nanorods. This was essential for the understanding of the structure of the rods and the interpretation of DF and BF image contrast as well as variations in the EDS signal. Similar 3D information was also available from more advanced techniques such as EFTEM (more noisy) thickness mapping or SI (less noisy).

![Figure 4](image)

Figure 4: (a) BF image of rod. (b) SI (grey) and EFTEM (black) thickness profiles and (c) EDS linescan signal of two places along the rod (X-X (top) and Y-Y (bottom) in figure a), showing a clear correlation between the EDS signal and the shape of the rod.

5. Conclusion
Detailed TEM characterization of PbTiO₃ nanorods has been performed to reveal the shape, the growth direction and the internal structure of the rods. This was achieved by two different sample preparation methods providing a side-view as well as a cross-section view of the rods which, combined with thickness mapping techniques, provided a 3D view. The defects in the rods, such as tunnels, rotation of building blocks creating internal defects and surface steps, affected both BF and DF contrast and the EDS measurements and must be fully characterized before attempting to resolve the ferroelectric domain structure of the rods.

References
[1] G. Wang et al. J. Nanosci. Nanotechnol. 7, 2538 (2007).
[2] G. Wang et al. Chem. Mater. 19, 2213 (2007).
[3] See for example H. Cölfen and M. Antonietti. Angew. Chem. Int. Ed. 44, 5576 (2005).
[4] M Tanaka. Acta cryst. A 31, 59 (1975).