Study of titanate nanotubes by X-ray and electron diffraction and electron microscopy

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ABSTRACT

The structure of titanate nanotubes (Ti-NTs) was studied by a combination of powder X-ray diffraction (PXRD), electron diffraction and high resolution transmission electron microscopy (HRTEM). Ti-NTs are prepared by hydrothermal treatment of TiO_2 powder. The structure is identified by powder X-ray diffraction as the one based on the structure of $H_2Ti_2O_5 \cdot H_2O$ phase. The same structure is obtained by projected potential from HRTEM through-focus image series. The structure is verified by simulated PXRD pattern with the aid of the Debye formula. The validity of the model is tested by computing Fourier transformation of a single nanotube which is proportional to measured electron diffraction intensities. A good agreement of this calculation with measured precession electron diffraction data is achieved.

1. Introduction

Recently, high interest has been given to titanate (titania) nanotubes (Ti-TNs) in particular, due to their potential use in different applications. Ti-NTs can be used in many applications where TiO_2 powders are utilized nowadays. However, the advantage of utilizing Ti-NTs is mainly due to their elongated structure assisting the electron transport. Bavykin and Walsh [1] discussed their possible uses in dye sensitive solar cells, lithium batteries, photocatalysis, magnetic materials, hydrogen storage or covering orthopedic or dental implants.

Unfortunately, the structure of Ti-NTs has not been clearly understood yet. An inexpensive method of preparation of

Ti-NTs was described by Kasuga [2]. The preparation is based on a hydrothermal treatment of TiO_2 powder with NaOH. That publication initiated quite a huge interest on Ti-NTs and also the discussion about their structure. Kasuga [2] reported the structure of Ti-NTs as the one of anatase. Other structures based on TiO_2 phases were reported by Deng [3] as brookite structure and by Armstrong [4] as beta TiO_2 phase. On the other hand, Chen [5] showed that the structure of Ti-NTs could possibly be assigned as $H_2Ti_3O_7$. The tubular structure could not be obtained by just replacing NaOH by LiOH or KOH in the synthesis. The authors [5] removed Na ions from the structure by washing it in H_2O. Another reported structure of Ti-NTs was $H_2Ti_2O_5 \cdot H_2O$, by Chen [6]. The authors studied the necessary time for obtaining Ti-NTs. The final tubular structure was obtained after 20 h of reaction time and the resulting Ti-NTs had a multiwall structure with four walls. The structure of Ti-NTs was related to the one of $Na_2Ti_2O_5 \cdot H_2O$ and it

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was possible to remove Na ions [7]. Nakahira [8] suggested that the possible structure of Ti-NTs was $H_2Ti_4O_9 \cdot H_2O$. The authors studied the influence of the structure of TiO_2 initial powder on the structure of Ti-NTs. They used different initial powders: anatase TiO_2 powder, a mixture of anatase and rutile TiO_2 powder (3:1) and rutile TiO_2 powder. Surprisingly, they found that all powders gave the same final structure of Ti-NTs. By replacing NaOH by KOH the $H_2Ti_4O_9 \cdot H_2O$ structure of Ti-NTs was formed. The nanotube had a diameter of about 10 nm. The sodium salt (for example $Na_2Ti_2O_5 \cdot H_2O$) of these structures could be found as well if the sample was not well washed and some sodium ions are still presented.

Our aim was to find the structure of Ti-NTs prepared by the hydrothermal method. In order to accomplish this task, a combination of three complementary methods: powder X-ray diffraction (PXRD), high resolution transmission electron microscopy (HRTEM) and electron diffraction (ED) was used. A computer simulation of PXRD pattern utilizing the Debye formula was used for the structure verification. The intensity distribution in the calculated Fourier transformation of the single nanotube based on model is comparable to that of precession electron diffraction.

Fig. 1 – SEM image of nanotubes.

2. Methods

The investigated Ti-NT samples were prepared by hydrothermal treatment of nanocrystalline TiO_2 anatase powder. The powder was dispersed in 10 M NaOH aqueous solution. This suspension was put into a closed vessel and heated at 120 °C for 48 h. After the synthesis, the sample was washed and neutralized by HCl. In order to obtain powder samples of Ti-NTs, the sample was freeze-dried.

The structure investigations were performed by three complementary methods: X-ray diffraction (XRD), HRTEM and ED.

The XRD is a widely used method for structure determination. The X-ray measurements on the Ti-NT samples were performed on a PANanalytical MPD diffractometer with the $CuK\alpha$ radiation. The sample was mixed with a solvent and spread on a glass or the so-called non-diffracting Si substrate holder. The sample was measured in the Bragg–Brentano geometry with variable slits and the PIXcel detector, in the 2θ range from 5° to 80°. Powder diffraction patterns were measured with the step size of 0.0263° 2θ; total integrating time for one step was 180 s. Incident beam was conditioned by Soller slit (divergence 0.04 rad) and a beam mask of width 5 mm was used. Automatic divergence slits were used both in primary and diffracted beam in order to achieve constant irradiated area during measurement (5×8 mm^2.) In front of the PiXCel detector (in scanning mode), Soller slits (0.04 rad divergence) and a beta-filter (Ni) were placed.

PXRD gives information on the crystalline structure averaged over irradiated volume. On the other hand, HRTEM can be used to visualize the structure of a single nanotube. One of the challenges of this study was to find the required single nanotube because nanotubes prefer to stick together as shown in Fig. 1.

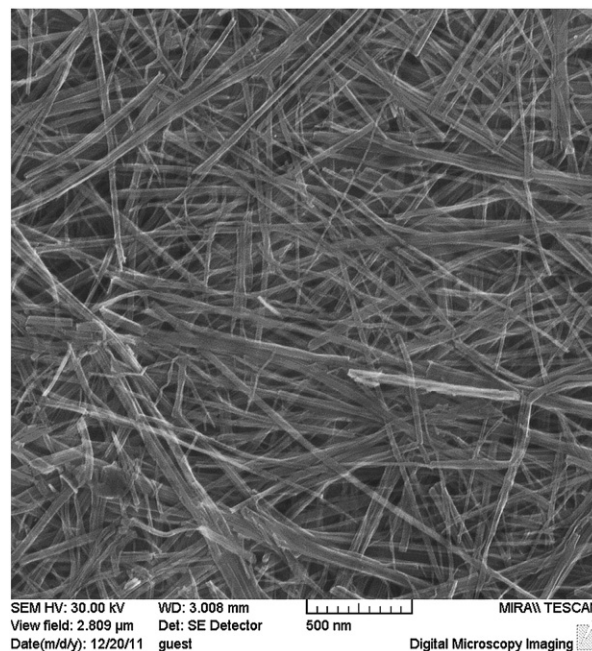Ti-NTs were ultrasonically dispersed in ethanol and then a drop of the sample was spread on a holey carbon-coated microscope copper grid. Individual nanotubes were studied by HRTEM imaging, performed on JEOL JEM 2100 F FEG (field emission gun) operated at 200 kV accelerating voltage.

A through-focus series of HRTEM images consisting 20 images at different defocus values were taken. These images were corrected for distortions by contrast transfer function (CTF) and the individual CTF-corrected images were combined into a reconstructed image of structure using the structure projection reconstruction method [9].

ED patterns were collected on the single nanotube as well. As the interaction of electrons with matter is ~104 times stronger than that for X-rays, dynamical effects should be taken into account and the interpretation of ED patterns is more complicated than that of XRD patterns. In order to overcome this problem, digital precession electron diffraction (PED) [10] was used to collect ED data. In this method the electron microscope is controlled by dedicated software only. The electron beam is rotated along a circle at a certain angle (so-called precession angle; 2° in this work) around the optical axis of the microscope. The beam rotation along the circle is sampled with a fixed azimuthal step (3° in this work) which results in 120 individually beam-tilted ED patterns. These patterns are combined into the final PED pattern by (1) aligning all patterns against each other using cross-correlation and (2) summing up the aligned patterns. The set of structure factors extracted from the final PED pattern is closer to kinematical intensities.

PED patterns were recorded on JEOL JEM 2100 LaB$_6$ operated at 200 kV accelerating voltage. The sample preparation was the same as in for HRTEM imaging.

EDS was used for investigation of chemical compositions of the sample. EDS studies were performed on a Tescan Mira1 microscope. This microscope had auto emission electron gun operated at 15 keV. Scanning electron microscopy (SEM) studies were performed also on this microscope at 30 keV in

order to study the morphology of Ti-NTs. Commercial scanning electron microscope Mira I (Tescan) was used for SEM and EDS investigations. The microscope use EDS Bruker Quantax 800 analyzer equipped with detector XFlash 6|10 with energy resolution 129 eV. Samples were placed on carbon tape in the case of EDS. For SEM measurement the samples were put directly on the aluminum sample holder without coating. No charging effect was observed during measurements.

3. Results and Discussion

Energy dispersive X-ray spectroscopy (EDS) was first performed in order to find whether the samples may have the structure of TiO_2 or one of the titanium salts. EDS analysis revealed certain contents of sodium ions and thus the structure was assumed to be one of the titanium salts. The result of EDS is shown in Table 1. where only Ti K-edge and Na K-edge were given.

The following titanium acids $H_2Ti_4O_9 \cdot H_2O$, $H_2Ti_3O_7$ and $H_2Ti_2O_5 \cdot H_2O$ are selected from database and the theoretical positions of diffraction lines for each of them were compared with measured PXRD pattern. This comparison is shown in Fig. 2.

The best match was achieved for the $H_2Ti_2O_5 \cdot H_2O$ phase with an orthorhombic structure and the unit cell parameters:

$$a = 18.03 \text{ Å}, \quad b = 3.78 \text{ Å}, \quad c = 2.998 \text{ Å}.$$

The predicted structure from PXRD analysis should be that of $Na_xH_{2-x}Ti_2O_5 \cdot H_2O$ where the content of sodium ions × is determined from EDS to be 0.4.

XRD gave information on the average crystalline structure of nanotubes. However we were also interested in the structure of a single nanotube. A through-focus series of HRTEM images was taken at different defocus values. The obtained picture is shown in Fig. 3. in which the black dots represent Ti–O octahedron.

Characteristic features of the nanotube are the following: a zig–zag shape on the edge of the nanotube and small squares in the middle of the tube. The distances between the atomic columns in the middle and on the edge could be found from the reconstructed structure image. To obtain the distances more accurately, 10 dots in the edge and in the middle of the tube were measured. Both measured distances are illustrated in Fig. 3. The distance of 38 Å was measured on the edge of the nanotube and so one lattice parameter should be 3.8 Å. In the middle of the tube, the obtained distance was 30 Å—the other lattice parameter should be 3 Å. These
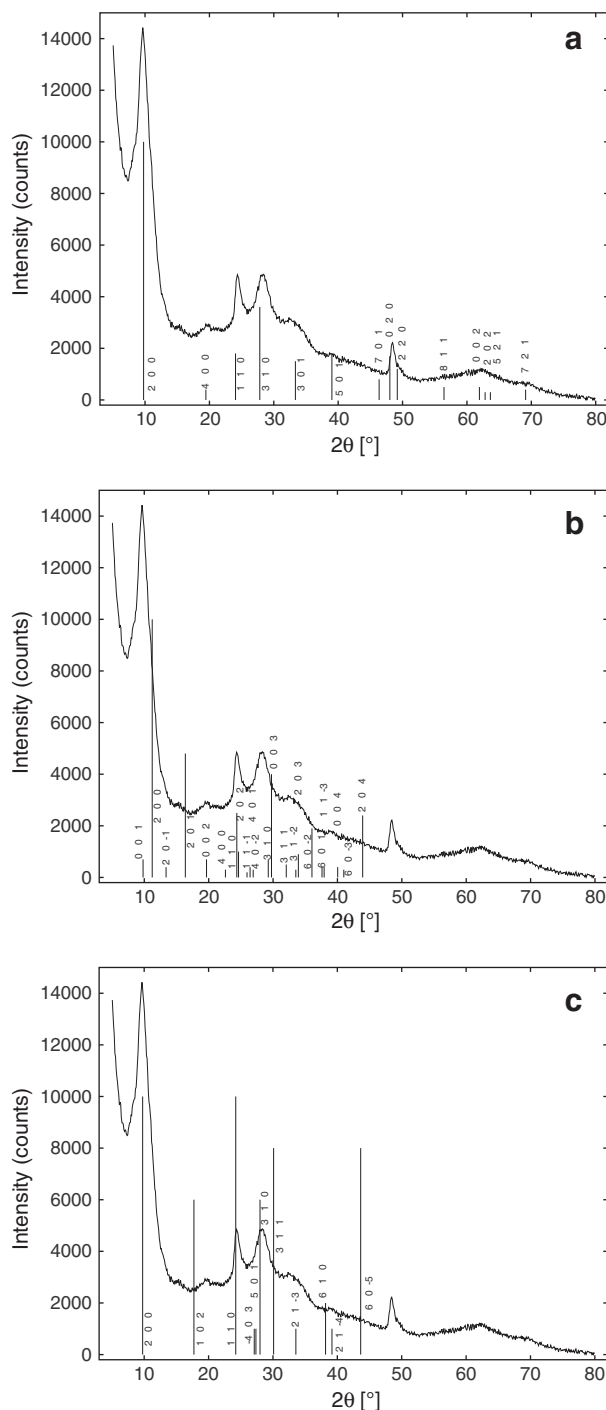

Fig. 2 – a—Comparison of measured XRD powder pattern and theoretical positions of diffraction peaks of $H_2Ti_2O_5 \cdot H_2O$ phase. b—Comparison of measured XRD powder pattern and theoretical positions of diffraction peaks of $H_2Ti_3O_7$ phase. c—Comparison of measured XRD powder pattern and theoretical positions of diffraction peaks of $H_2Ti_4O_9 \cdot H_2O$ phase.

distances are compared with the structure suggested from PXRD—$H_2Ti_2O_5 \cdot H_2O$. The distance in the 'zig–zag' edge corresponds to cell parameter b of this structure. The second measured distance corresponds to the lattice parameter c of

Table 1 – EDS analysis of Ti-NTs. The abbreviation 'atom. C [%]' means atomic concentration of given element, 'nor. C [%]' denotes weight concentration. Reported errors are the total errors according to the statistical treatment of the data.

Element	Nor. C [%]	Atom. C [%]	Error [%]
Titanium K-series	91.2	83.3	2.1
Sodium K-series	8.8	16.7	0.5
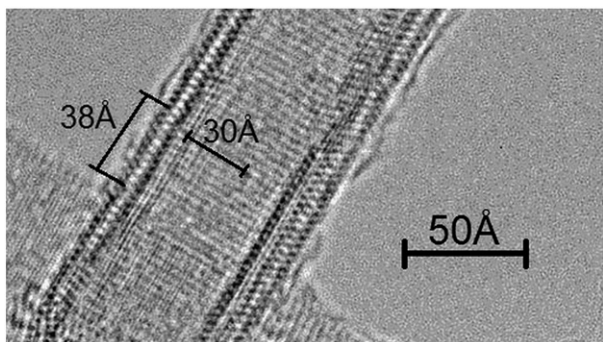
Fig. 3 – The structure image reconstructed from the through-focus series.

Fig. 4 – Side view of the model of nanotube—only Ti atoms shown (displayed by [12]).

this structure. Therefore, we assume that Ti–NT has the structure of $H_2Ti_2O_5 \cdot H_2O$ and it is possible to orient the unit cell with respect to the nanotube as follows: the c axis is directed around the nanotube circumference, the b axis is along the direction of the nanotube axis and a axis is directed perpendicular to the center of the tube.

In order to verify the orientation of Ti-NTs it was necessary to create a model, simulate the PXRD and ED patterns and compare them with the experimental data. The atom positions in the unit cell of $H_2Ti_2O_5 \cdot H_2O$ have been published [7], but unfortunately the positions of water molecules were not correct in this model. Thus for our computer simulation a model based on the structure of $(H_3O)_{0.11}Cs_{0.24}Ti_{0.91}O_2(H_2O)_{0.12}$ presented [11] was used. It is also orthorhombic just like $H_2Ti_2O_5 \cdot H_2O$ and the lattice parameters are very similar. Only Ti–O octahedron from the structure [11] was used for our calculations because they create the main building blocks in titanates. In order to have correct numbers of titanium atoms in the calculations, because used structure $(H_3O)_{0.11}Cs_{0.24}Ti_{0.91}O_2(H_2O)_{0.12}$ has only one Ti atom unlike our predicted structure $H_2Ti_2O_5 \cdot H_2O$ having two Ti atoms, the z positions of titanium and oxygen atoms were replaced. The nanotube has a spiral base as can be seen in Fig. 3. There are two walls on the left side and three on the right—the nanotube is made by a rolling 2D sheet. The first step in our computer simulation was to build a model. The radius of nanotube is one necessary parameter of the model and it could be estimated from the HRTEM image. The inner diameter of the nanotube is 53.8 Å. The second important parameter of the model is the distance between walls. This distance could not be obtained from HRTEM images because the high vacuum could decrease the distance. Thus the distance from the HRTEM image was taken as the first approximation and then the PXRD pattern was calculated with the aid of the Debye formula and compared with the experimental one. This was repeated for several values of the parameter until a reasonable match was achieved. The distance between walls was changed in the model in order to obtain a good match of the first diffraction peak position. This peak corresponds to the direction of stacking walls as can be seen in Fig. 2. The final value of distance between the walls of Ti-NT obtained by calculations—approximately 8.3 Å—is in good agreement with the value reported by Nakahira [8] which is 9 Å or less.
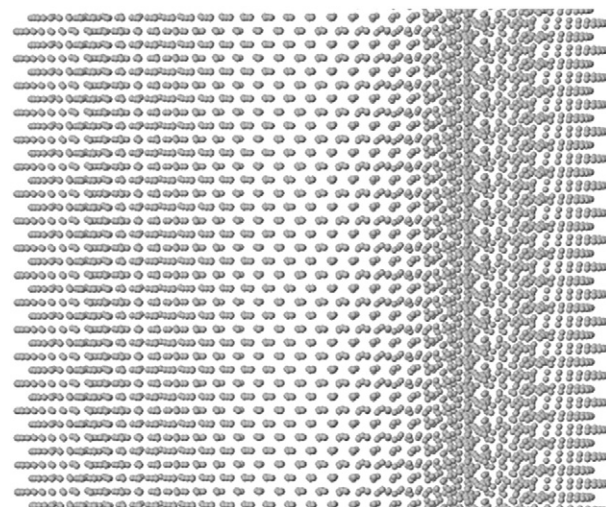
A side view of the Ti-NT with only Ti atoms is presented in Fig. 4.

The 2D Fourier transformation of this view was calculated and compared with the diffraction pattern measured by precession ED. The squared amplitudes of the Fourier transformation are proportional to the intensities in diffraction pattern. Relatively good correspondence of the Fourier transformation and the experimental ED pattern is shown in Fig. 5.

XRD pattern of a nanotube can be computed by means of the Debye formula [13]. In this formula the sum over all atomic pairs must be calculated:

$$I_{eu} = \sum_i \sum_j f_i f_j \frac{\sin q r_{ij}}{q r_{ij}}, \qquad (1)$$

where r_{ij} is distance between two atoms, f_i, f_j the atomic scattering factor of atom i, j respectively and q is the diffraction vector magnitude, $q = \frac{4\pi}{\lambda}\sin\theta$. Formula (1) describes the intensity distribution of randomly oriented (nano)particles. The sum runs over all the pair distances r_{ij} of the atoms i, j. Unfortunately, the summation is very time consuming and one have to apply certain approximations. One of widely used numerical methods is based on using histograms of distances between the atoms. In the case of Ti-NT three histograms must be calculated—the first one from the positions of only Ti atoms, the second one from Ti and O atoms and the last one from oxygen atoms. Then, the Debye formula changes to the following:

$$I_{eu} = \sum_i N_i f_{Ti} \frac{\sin q r_i}{q r_i} + \sum_j N_j f_O \frac{\sin q r_j}{q r_j} + \sum_k N_k f_{Ti} f_O \frac{\sin q r_k}{q r_k} \qquad (2)$$

where $N_{i,j,k}$ is the frequency of positions in each histogram. Formula (2) speeds up the calculation more than a thousand-times.

The best agreement between the calculated and experimental PXRD patterns is shown in Fig. 6.

As it can be seen, the computer simulation of PXRD pattern has the same basic characteristic peaks as the experimental
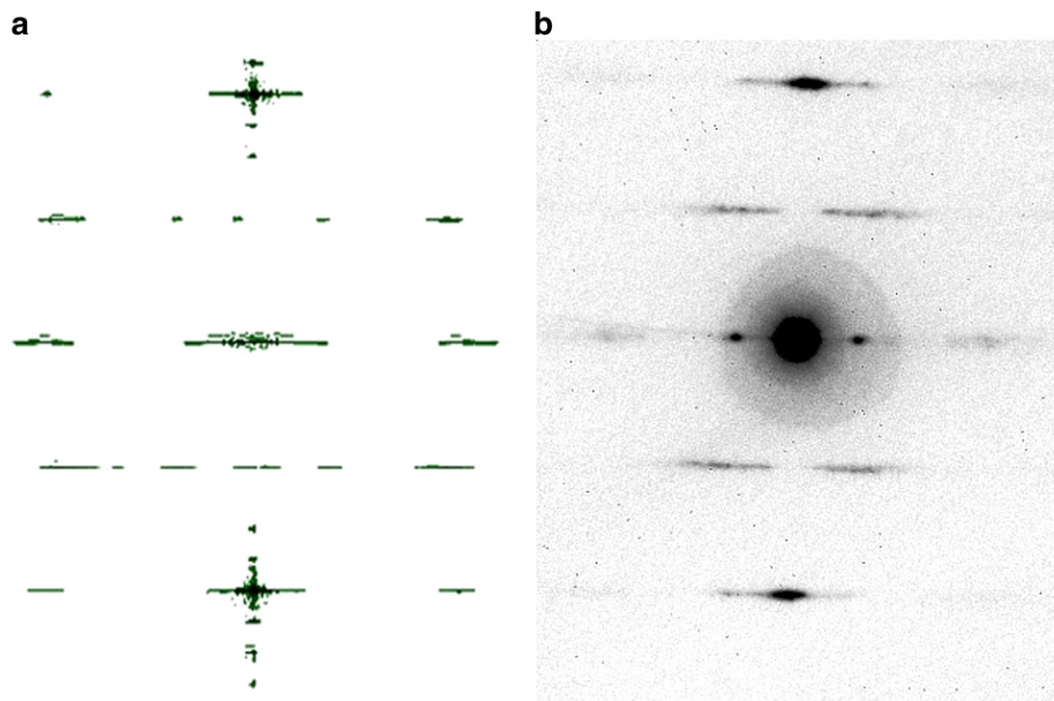
Fig. 5 – Fourier transformation of nanotube (left) and recorded ED pattern (right).

PXRD pattern. The main disagreement can be seen on the peak at about 2θ = 40°. This could be caused by neglecting possible preferred orientations of nanotubes in the calculations. Our specimens for PXRD in reflection mode were prepared on glass substrate. It is very probable that the nanotubes were lying on the holder so that in symmetrical Bragg–Brentano diffraction they can be hardly seen along the b axis. Preliminary studies of preferred orientation with the aid of the Eulerian cradle showed significant changes of the diffraction pattern with the specimen inclination and the narrow diffraction peak 020 increased with the sample

inclination. Therefore, in the next investigation we will include preferred orientation in the calculation with the Debye formula.

4.   Conclusions

The structure of titanate nanotubes prepared by the hydrothermal method was identified to be related to the structure of $Na_xH_{2-x}Ti_2O_5 \cdot H_2O$. This was approved by the comparison of powder X-ray diffraction pattern calculated via the Debye formula with the experimental data, the comparison of the Fourier transformation of the model with the experimental precession electron diffraction pattern and also from the structure image reconstructed from a series of HRTEM images. For improving the agreement of the simulated and experimental X-ray diffraction patterns, it is suggested that the effect of preferred orientation of nanotubes on the substrate holder should be considered and accurate atomic positions in the nanotubes should be determined as well.
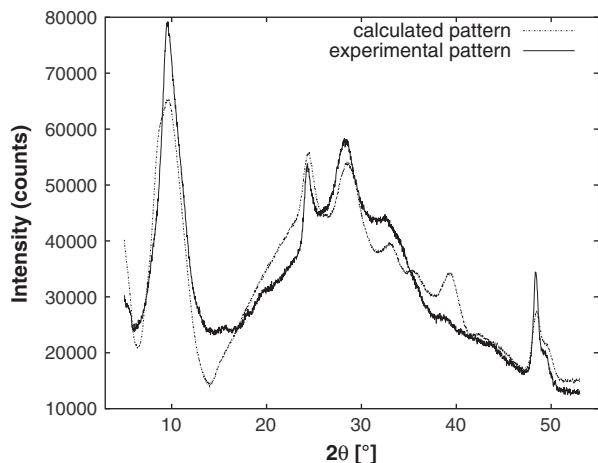
Fig. 6 – Comparison of measured and calculated XRD powder patterns.

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