

**MS39-04** Study of Titanate Nanotubes by X-ray and Electron Diffraction and Electron Microscopy. Tereza Brunatova,<sup>a</sup> Daniela Kralova,<sup>b</sup> Wei Wan<sup>c</sup>, Peter Oleynikov<sup>c</sup>, Miroslav Slouf<sup>b</sup>, Stanislav Danis<sup>a</sup>, Xiaodong Zou<sup>c</sup>, Radomir Kuzel<sup>a</sup> <sup>a</sup>Charles University in Prague, Faculty of Mathematics and Physics, Czech Republic, <sup>b</sup>Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic, <sup>c</sup>Stockholm University, Department of Materials and Environmental Chemistry, Stockholm, Sweden  
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Titanate nanotubes (Ti-NT) are relatively new material with many possible applications [1]. However, their structure is still not completely clear. The first suggested structure was anatase structure of TiO<sub>2</sub> [2]. Another structural model was created from the monoclinic β-TiO<sub>2</sub> phase [3] and the rest of published structures was based on the phases of titanium acids or sodium salts: H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> [4], H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>·H<sub>2</sub>O [5], H<sub>2</sub>Ti<sub>2</sub>O<sub>5</sub>·H<sub>2</sub>O [6], H<sub>2</sub>Ti<sub>4</sub>O<sub>9</sub>·H<sub>2</sub>O [7]. Sodium ions can be present in the structure of Ti-NT because Ti-NT are created via hydrothermal treatment of TiO<sub>2</sub> powder with NaOH solution. Ti-NT synthesised by hydrothermal method were studied by complementary methods - powder X-ray diffraction (PXRD), high-resolution transmission electron microscopy (HRTEM) and electron diffraction (ED). Several models were considered and tested. Finally, an optimal model was found by the combination of the above techniques. The basic features of PXRD pattern corresponded to the orthorhombic H<sub>2</sub>Ti<sub>2</sub>O<sub>5</sub>·H<sub>2</sub>O phase (or Na<sub>2</sub>Ti<sub>2</sub>O<sub>5</sub>·H<sub>2</sub>O since Na ions were detected in the samples) found in PDF-4+ database with the lattice parameters:  $a = 18.08 \text{ \AA}$ ,  $b = 3.797 \text{ \AA}$ ,  $c = 2.998 \text{ \AA}$ . The nanotubes are oriented in the following way: the axis of the nanotube is along the direction of  $b$ -axis and the lattice  $c$ -axis is along the circumference of the nanotube and  $a$ -axis is directed to the center. The inner diameter of the nanotube is approximately 53.8 Å, determined from through-focus HRTEM images. The model was created by rolling of a 2D sheet of Ti-O octaetra according to HRTEM. In cross-section, it gives a spiral with two and three layers, respectively. The distance between the layers is around 9.2 Å as estimated from PXRD pattern. The Fourier transformation of the model corresponds well to the precession ED. This model was used for the calculation of PXRD pattern with the aid of the well-known Debye formula and relatively very good agreement with experimental data was achieved. Some discrepancies are probably related to preferred orientation of nanotubes in the specimen for XRD experiment as verified by measurements with the Eulerian cradle.

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**MS39-05** Electron diffraction structure analysis of organic nano sized crystals Ute Kolb, Tatiana E. Gorelik, *Institut für Physikalische Chemie, Johannes Gutenberg Universität, Germany*,  
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Powder X-ray diffraction technique and electron diffraction are particularly interlinked methods since they can address exactly the same material and deliver different kind of structural information. Powder X-ray data gives information about the bulk sample, whereas electron diffraction can deal with individual crystals “seeing” them as single crystals. Through the combination of the two techniques complementary information can be obtained facilitating structural analysis.

Structure analysis of organic powders is often challenging for powder X-ray diffraction due to poor crystallinity, low symmetry, long lattice parameters, preferred orientation, and possible disorder effects. Electron diffraction can help resolving these problematic cases, furthermore, as each crystal is studied separately, polyphasic systems do not represent a specific problem. A severe limitation when investigating organic materials with electrons is the electron beam damage. Therefore, special techniques (ADT [1, 2] + electron dose distribution, cooling) are used in order to preserve the material during investigation.

High completion and resolution electron diffraction data sets allow ab-initio structure solution of organic materials for relatively complex systems. The structure analysis procedure is demonstrated for two oligo p-benzamides OPBA3 and OPBA4 [3]. The structure of OPBA3 was known initially and was used as a test for the method. The tested structure analysis route was then applied to a new structure of OPBA4.

Due to significant material damage during electron radiation, collection of high-resolution data for structure analysis is a very challenging task. Often obtaining a unit cell metric from nanocrystals can already resolve a crystallographic problem. Unit cell parameter determination and thereafter identification of the polymorph is demonstrated for hexagonal caffeine crystals [4].

Generally materials with long crystallographic axes are problematic for X-ray powder diffraction technique. Long lattice parameters through electron diffraction is demonstrated for dragon-fly PAH and triazine crystals.

Finally, stacking fault like disorder can be easily identified within reconstructed 3D electron diffraction reciprocal volume, allowing determination of the stacking fault direction and crystallographic description of the stacking shift vectors.

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