Structural investigations of nanocrystalline TiO_2 samples

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TiO_2 is used in many applications such as photovoltaic devices, integrated wave guides, gas and humidity sensors, inorganic membranes, catalyst supports and electrochemical displays [1, 2]. Two kinds of nanocrystalline TiO_2 samples were synthesized by the sol-gel method: iron doped TiO_2 (containing iron as a solid solution and poly(ethylene)glycol) and undoped TiO_2. The former sample exhibits the anatase modification, while the latter also contains, besides anatase (74 %), a small amount of brookite (26 %). Samples were characterized by means of X-ray diffraction (XRD) at room temperature using a Philips powder diffractometer (PW 1820) with monochromatized Cu$K\alpha$ radiation. Transmission electron microscopy (TEM) investigations were carried out by using a JEOL JEM 2010 200 kV microscope, (Cs=0.5 mm, point resolution 0.19 nm) with a beryllium window energy-dispersive (EDS) detector. The Rietveld refinement of X-ray diffraction (XRD, R_{wp}=10 %) and selected area electron diffraction (SAED, R_{wp}=15 %) methods were used in order to extract structural parameters of TiO_2 using the FULLPROF program [3]. The crystal structure was refined in the space group of anatase $I4_1/amd$ (141) and in the space group of brookite *Pbca* (61). The dependence of the lattice parameters of anatase on the grain size and average microstrain were determined. The lattice parameter *a* increased while the parameter *c* decreased with decreasing of the grain size, while the unit cell volume was almost constant. The Debye-Waller parameters *B* for our samples were enhanced in comparison with previous results obtained from neutron diffraction on coarse-grained TiO_2 powders (anatase) [4]. Significant differences of lattice parameters, bond lengths and angles were found between undoped and iron doped samples. The size-strain analysis was performed using the Rietveld method, and assuming that both size broadening and microstrain broadening are of Lorentzian profile type. The average microstrain decreased with the increase of the treatment temperature from 1.2 % for as prepared undoped sample to 0.67 % for annealed sample at 500^0C.

[1] J. Moser, M. Grätzel, R. Gallay, Helvetica Chimica Acta **70** (1987) 1596.
[2] A. Turković, A. M. Tonejc, S. Popović, P. Dubček, M. Ivanda, S. Musić, M. Gotić, Fizika **A6** (1997) 77.
[3] J. Rodriguez-Carvajal, FULLPROF-A program for Rietveld Refinement, Laboratorie Leon Brillouin, CEA-Saclay, France (2000).
[4] C. J. Howard, T. M. Sabine, F. Dickson, Acta Cryst. **B47** (1991) 462-468.