subjects with various parameters of their microstructure (sizes of microparticles, specific surface) and substructure (sizes of nanoparticles and crystallites) governing their working properties.

The purpose of the work is to find correlations between synthesis conditions of samples with nanosized η-TiO_2, their characteristics and structural, sorption, catalytic and photocatalytic properties.

The determination of η-TiO_2 cell parameters (a~3.8Å, c~19Å) has been made using sources of electrons, X-rays and synchrotron scattering. These parameters are associated with ones of anatase modification (a_0~3.8Å, c_0~9.5Å) by the relationship $a \sim a_0$, $c \sim 2c_0$. Optimization of the sulfate method allowed increasing the yield of η-TiO_2 up to 95%. The samples were characterized by a set of methods showing variations in sizes of microparticles/ agglomerates (200/3000 nm; SEM, BET), nanoparticles (8÷24 nm, rarely 28÷55 nm; small angle X-ray scattering), crystallites, or coherent scattering regions (L=3÷6 nm; large angle X-ray scattering), as well as in sizes (~17 nm; BET) and capacities (0.02 cm^3/g; BET) of pores and specific surface (4.5÷16 m^2/g; BET). Dependence of some parameters (in particular, value L) on synthetic conditions (the initial concentration of $TiOSO_4 \cdot x H_2SO_4 \cdot y H_2O$ reagent, the temperature and duration of hydrolysis, the heating speed of reaction mixture and so on) was found.

Photocatalitic activity (in model reactions of decomposing methyl-orange, methylene-blue and xylenol-orange indicators under UV radiation), sorption properties (extraction of various ions from aqueous media) and catalytic properties (oxidation of CO to CO_2 in air at room temperature) depend on sample characteristics. Efficiency of CO conversion to CO_2 correlates with specific surface. For bismuth, arsenic and vanadium ions, degree of sorption equal to maximal permissible concentration was achieved. A relation between the degree of metal-ion sorption and the coherent scattering regions (value L) has been established. Degree of metal-ion sorption and rate constant for photocatalytic reactions are maximal for L ~ 4.5 nm. Photocatalytic activity (pH < 3) for the samples with η-TiO_2 is considerably higher than for commercial photocatalysts Degussa P25 (anatase–rutile mixture) tested in comparable conditions. The photocatalytic and catalytic activities obtained confirm unique surface properties of η-TiO_2.

From the X-ray diffraction study data by means of crystallochemical approach, the structure of η-TiO_2 was proposed. The quasi-layered structure model provides a very fit to the experimental data (in particular, the sorption properties).

Keywords: nanosized η-TiO2, (micro)structure, properties

MS18.P06

Acta Cryst. (2011) A**67,** C323

(Micro)structure determination of ferrite nanoparticles using multiple techniques

Bratislav Antic,[a] Aleksandar Kremenovic,[a] Natasa Jovic,[a] Jovan Blanusa,[a] Bostjan Jancar,[b] Emil S. Bozin,[c] *[a]Laboratory for Condensed Matter Physics, Institute of Nuclear Sciences "Vinca, Belgrade, (Serbia), [b]Advanced Materials Department, Institute "Josef Stefan", Ljubljana (Slovenia), [c]Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, NY (USA)* E-mail: bantic@vinca.rs

We report results of systematic studies utilizing multiple techniques on series of two nanoparticle ferrite systems, $ZnFe_2O_4$ and $Li_{0.5}Fe_{2.5}O_4$, obtained using variable thermal annealing protocols. Details of structure and microstructure changes of ferrite nanoparticles are assessed using synchrotron X-ray and TOF neutron diffraction data by combining Rietveld method in reciprocal space with the atomic pair distribution function (PDF) method in direct space. Such obtained (micro)structural parameters were correlated with physical properties revealed by HRTEM, Mössbauer spectroscopy and DC magnetization.

Small discrepancies between Rietveld and PDF results were found for the values of lattice parameters of $ZnFe_2O_4$, in which case those derived from PDF can be considered as more reliable. Refined occupation number of Zn ions, as determined by Rietveld refinement, reveals change of occupation ratio over tetrahedral and octahedral sites within the space group Fd-3m. The results show that bulk sample resembles a normal uninverted spinel structure, while there is about 25% of inversion found in as-prepared sample (S1) and annealed sample at 300 ºC (S2). This is in good agreement with results obtained from Mössbauer spectroscopy, where degree of inversion was found to be 27%. With further annealing at 400 ºC (S3) inversion drops to 16%.

Particle size and microstrain were determined using isotropic (spherical) particle shape model and isotropic microstrain (random defects distribution). This resulted in crystallite size values of 3.4 nm (S1), 7.7 nm (S2), and 13 nm (S3), in good agreement with those obtained from PDF and HRTEM analyses. These results further indicate a tiny shell, in agreement with DC magnetization data that suggest negligible interaction between magnetic moments in nanoparticle core and shell. The coercivity and blocking temperature were found to increase with increasing crystallite size.

Crystal structure and microstructure evolution of $Li_{0.5}Fe_{2.5}O_4$ nanoparticles obtained after annealing at 180, 300 and 400 ºC were also studied. The 5-10 nm particles exhibit similar crystal structure, on average, with a partial ordering of Li^+ and Fe^{3+} ions between octahedral 4*b* and 12*d* sites on the spinel crystal lattice (space group $P4_332$). PDF analysis reveals an anomalous increase of the oxygen O1 isotropic atomic displacement parameters to unphysical values, suggesting significant disordering within the O1 network. Since the nearest neighbor coordination of the iron in tetrahedral sites is much more influenced by the oxygen O1 anions than the octahedral sites in spinel structure, it can be concluded that thermal annealing of lithium ferrite powder mainly activated relaxations of the oxygen sublattice and does not change significantly the cation distribution up to 400 ºC.

The SNF has financially supported this work under SCOPES project (Grant No. IZ73Z0_1 27961). Work at BNL was supported by the U.S. DOE-BES under contract DE-AC02-98CH10886.

Keywords: nano -1, powder -2, magnetic -3

MS18.P07

Acta Cryst. (2011) A**67,** C323-C324

NiO/Ni nanocomposite (micro)structure evolution induced by thermal annealing and milling

Aleksandar Kremenović,[a,b] Bratislav Antić,[b] Milica Vučinić-Vasić,[c] Mira Ristić,[d] Boštjan Jančar,[e] and Jelena Rogan,[f] *[a]Faculty of Mining and Geology, University of Belgrade (Serbia) [b]Institute of Nuclear Sciences "Vinca", Belgrade (Serbia), [c]Faculty of Technical Sciences, University of Novi Sad (Serbia), [d]Ruđer Bošković Institute, Zagreb (Croatia), [e]Institute "Jožef Štefan", Ljubljana (Slovenia), [f]Faculty of Technology and Metallurgy, University of Belgrade (Serbia).* E-mail: akremen@EUnet.rs

There is an increasing interest in the last few years for studies of ferromagnetic (FM) - antiferromagnetic (AFM) systems because of exchange coupling between FM and AFM phases that influence on physical properties as well as unresolved scientific issues. Therefore, there is a challenge to find a simple and controlled procedure for preparation of FM-AFM nano systems with technological impact. Although, the process of thermal decomposition of nickel(II) acetate tetrahydrate was described in literature, we performed an integrated study of it by different techniques.