

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 -TiO₂, their characteristics and structural, sorption, catalytic and photocatalytic properties.

The determination of η -TiO₂ cell parameters ($a \sim 3.8 \text{ \AA}$, $c \sim 19 \text{ \AA}$) has been made using sources of electrons, X-rays and synchrotron scattering. These parameters are associated with ones of anatase modification ($a_0 \sim 3.8 \text{ \AA}$, $c_0 \sim 9.5 \text{ \AA}$) by the relationship $a \sim a_0$, $c \sim 2c_0$. Optimization of the sulfate method allowed increasing the yield of η -TiO₂ 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 ($L = 3 \div 6$ nm; large angle X-ray scattering), as well as in sizes (~ 17 nm; BET) and capacities (0.02 cm³/g; BET) of pores and specific surface (4.5÷16 m²/g; BET). Dependence of some parameters (in particular, value L) on synthetic conditions (the initial concentration of TiOSO₄· x H₂SO₄· y H₂O reagent, the temperature and duration of hydrolysis, the heating speed of reaction mixture and so on) was found.

Photocatalytic 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 CO₂ in air at room temperature) depend on sample characteristics. Efficiency of CO conversion to CO₂ 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 $L \sim 4.5$ nm. Photocatalytic activity (pH < 3) for the samples with η -TiO₂ 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 -TiO₂.

From the X-ray diffraction study data by means of crystallochemical approach, the structure of η -TiO₂ 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

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(Micro)structure determination of ferrite nanoparticles using multiple techniques

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We report results of systematic studies utilizing multiple techniques on series of two nanoparticle ferrite systems, ZnFe₂O₄ and Li_{0.5}Fe_{2.5}O₄, 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 ZnFe₂O₄, 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 °C (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 °C (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}O₄ nanoparticles obtained after annealing at 180, 300 and 400 °C were also studied. The 5-10 nm particles exhibit similar crystal structure, on average, with a partial ordering of Li⁺ and Fe³⁺ ions between octahedral 4b and 12d sites on the spinel crystal lattice (space group P4₃32). 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 °C.

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

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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.

Ni/NiO nanocomposite obtained by thermal decomposition of nickel(II) acetate tetrahydrate, $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, at 300 °C is composed from NiO (65%) and Ni (35%) with crystallite size of 18 nm and 91 nm, respectively. It was found increasing of crystallite size, decreasing microstrain and increasing NiO phase content with thermal annealing in air, while high energy ball milling leads to decrease of crystallite size, increase size of agglomerates and strain as well as reduction, $\text{NiO} \rightarrow \text{Ni}$. Lattice parameters of nanosize NiO and Ni show a deviation from the bulk value for counterparts as a consequence of crystallite size reduction and grain surface relaxation effect. Exchange bias found in milled sample with particles of 12.5 nm (NiO) and 16.5 nm (Ni) disappears for larger particles as a consequence of coupling area decrease between antiferromagnetic and ferromagnetic particles. Due to reduction/oxidation ($\text{NiO} \leftrightarrow \text{Ni}$) and size as well as surface relaxation effects saturation magnetization value increases/decreases with milling/annealing, respectively.

Having in mind found size effect on exchange bias, coercivity and magnetization values, it is possible by annealing/milling to tailor composition and particle size and then control exchange bias and improve other magnetic properties of Ni/NiO.

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Local environment of Co^{2+} ions intercalated in VO_x /hexadecylamine nanotubes

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The synthesis of nanostructures of oxides is an actual challenge among the scientific community. Many efforts are dedicated toward the development of material and structures with at least one dimension on the nanometer scale. One of these systems is the vanadium oxide nanotube (VO_x NT), which presents potential applications in catalysis and electrochemistry, as cathode of Li-ion batteries [1]. The VO_x NT's are a multiwall nanostructure, where the walls are constituted by alternated layers of VO_x and organic surfactant. The surfactant acts as template, providing support and hardness to the structure. The layers of VO_x are constituted by V ions in two oxidation states (4+ and 5+). The V^{4+} ions are essential for the rolling up of the VO_x layers, which form the NT. Unfortunately the presence of this ion reduces the performance of the cathodes. In this point appears the necessity of obtaining VO_x NT's where the amount of V^{4+} ions is reduced and the tubular shape is preserved.

With this aim, we have performed doping treatments with transition metal ions to VO_x /hexadecylamine (HDA) NT's, in order to study the influence of doping ions on the magnetic properties of the system. We found that the doping treatments with Co and Ni ions reduce significantly the content of V^{4+} keeping the tubular morphology. [2]

In this work we present a characterization of VO_x /HDA NT's doped with Co ions performed by Transmission Electron Microscopy (TEM), X-ray powder diffraction (XRPD) and X-ray absorption spectroscopy (XAS). The first result obtained by XAS was the corroboration of our magnetic and electron spin resonance results, where we assign

to the intercalated Co ions the 2+ oxidation state. This confirmation was obtained comparing the XANES (X-ray Absorption Near Edge Structure) spectra of our NT's with standards ($\text{LaCo}^{3+}\text{O}_3$, Co^{2+}O and metallic Co).

By XAS characterization we obtained the first image of the local environment of the Co^{2+} ions intercalated in the VO_x /HDA NT's. The cobalt ions are located in the region of the surfactant close to two oxygen atoms of the oxide layer.

[1] M.E. Spahr, P. Stoschitzki-Bitterli, R. Nesper, O. Haas, P. Novák, *J. Electrochem. Soc.* **1999**, 146, 2780. [2] M.E. Saleta, H.E. Troiani, S. Ribeiro Guevara, G. Ruano, R.D. Sánchez, M. Malta, R.M Torresi. *J. App. Phys.* **2011**, in press.

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Crystal size effects in NiO

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Nickel oxide powder was synthesized by the sol-gel technique: A concentrated ammonium hydroxide solution was added dropwise to 100 mL of a magnetically stirred aqueous 0.1 M NiCl_2 solution, until the pH was ca 9. A xerogel of nickel hydroxide was obtained after filtering the precipitated gel, washing with a little amount of water and leaving to dry in air. Fine nickel oxide powder of cubic halite-type structure was obtained after thermally annealing the xerogel in air for 3 h at a constant temperature, between 300 and 1300 °C. The crystal structure was determined by x-ray diffraction. The grain size was evaluated by broadening analysis of the diffraction spectra and verified by electron microscopy. It was found that the grain size is strongly affected by the firing temperature — larger grains were obtained at higher temperatures. At grain size below 40 nm the cell parameter started to increase as the grain size decreased. To avoid possible instrumental effects, powder diffraction data collected from two diffractometers working on entirely different principles were shown to be in good agreement (Fig. 1). One was a transmission Guinier diffractometer and the other one was a back-reflection scattering Bragg-Brentano system. The cell parameter for grains size above 40 nm was 4.1774 Å, fairly close to published data [1], [2] and without the slight rhombohedral distortion [3]. It is possible to explain the lattice expansion phenomenon in ceramic nanocrystals by a Madelung-type model, where the attraction potential between anions and cations is smaller in a small crystal than in a conventional bulk-sized one.

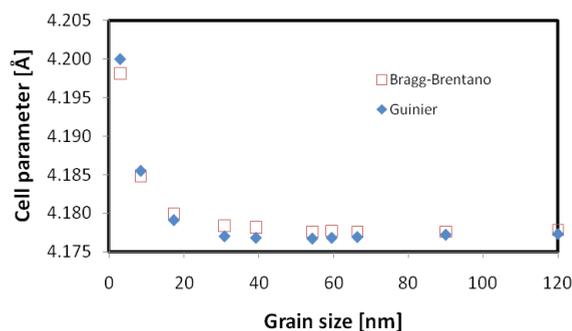


Fig. 1: Cell parameters as function of grain size, as determined from two different diffractometers.