

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

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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.

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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.

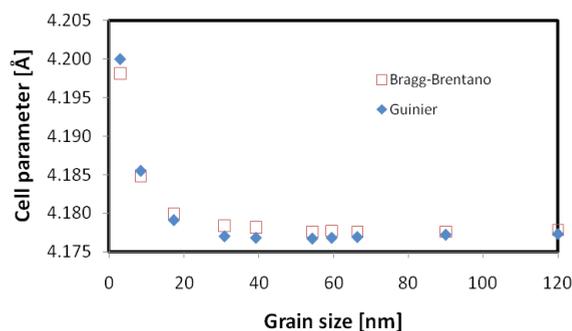


Fig. 1: Cell parameters as function of grain size, as determined from two different diffractometers.

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Crystallographical characterization of nanocrystals PbS doped with Ni

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The thin films of lead sulfide (PbS) doped with Ni have been successfully synthesized using chemical bath deposition (CBD) method. The films were deposited on glass substrate at temperature 80 ± 2 °C, using five different levels of doping Ni; 0, 2, 4, 6, 8, and 10 mLs. The structural characterization shows that the films are deposited on phase face-centered cubic and the decreases in grain size (TG) with increases of Ni concentration, from order 40 to 10 nm.

Keywords: crystallographical, nanocrystals, PbS

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X-ray scattering studies of amorphous and nanocrystalline pharmaceutical materials

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The increased interest in recent years regarding the properties and applications of amorphous and nanocrystalline materials has also created the need to characterize the structures of these materials. However, due to the lack of long-range atomic ordering, the structures of nanostructured and amorphous materials are not accessible by conventional diffraction methods used to study crystalline materials. One of the most promising techniques to study nanostructures using X-ray diffraction is by using the total scattering (Bragg peaks and diffuse scattering) from the samples and the pair distribution function (PDF) analysis. The pair distribution function provides the probability of finding atoms separated by a certain distance. This function is not direction-dependent; it only looks at the absolute value of the distance between the nearest neighbors, the next nearest neighbors and so on. The method can therefore also be used to analyze non-crystalline materials. From experimental point of view a typical PDF analysis requires the use of intense high-energy X-ray radiation ($E \geq 15$ KeV) and a wide 2θ range.

In this study we present PDF results obtained from several pharmaceutical materials (salbutamol sulfate, sulfamerazine and paracetamol) and discuss the applicability of the PDF analysis for structural characterization of amorphous and nanocrystalline materials with application in the pharmaceutical industry. The experimental

results presented in the poster were obtained using a standard laboratory X-ray diffraction system.

This study further demonstrates that PDF analysis with a laboratory diffractometer can be a valuable tool for structural characterization of nanomaterials.

Keywords: amorphous, nanocrystal, pharmaceutical

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A new method for measuring x-ray rocking curves by means of x-ray acoustooptics

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A new method for measuring angular distribution of X-ray beam diffraction intensity (method for measuring X-Ray rocking curves) is represented. Intensity distribution analysis in this method is conducted by ultrasonic modulation of a lattice parameter of X-ray acoustic crystal, used as an analyzer. The distinctive feature of this method is the possibility to lead precise and time-resolved measurements of X-ray rocking curves without using sophisticated goniometry system.

Special X-ray acoustooptics elements – X-ray acoustic resonators, consisting of a piezoelectric crystal (quartz) and X-ray optical crystal (silicone) was developed to implement the method. Piezoelectric crystal was used to create a standing acoustic wave and control effectively a tension-compression deformation in the X-ray optical crystal [1]. Developed X-ray optical scheme and optical elements allow us to create uniform (within X-ray beam footprint) time-variable deformation of crystal lattice [2] and use these X-ray acoustic resonators as analyzers of scattered X-rays beam.

Rocking curves, measured by proposed X-ray acoustic method by shape and halfwidth agrees well to curves measured according to traditional way - by rotating a crystal. Experimental results of method approbation - examples of rocking curves of (440) reflection silicon crystal and (220) paratellurite crystals measured on laboratory diffractometer using X-ray acoustic method will be presented. Fig.1. shows an X-ray optical scheme and DuMond diagram corresponding to this double-crystal scheme.

The angular and time resolution of the method is determined by speed of detecting apparatus (the minimum possible changing of phase and minimal width of stroboscopic window or number of channels of the multichannel scaler) and depends on parameters such as ultrasound frequency and amplitude of ultrasonic vibrations. Experimentally achieved resolution of the method is 0.1 arcsec. Accuracy can be increased no less than an order by using an ultra-fast multichannel scaler. Developed method and experimental schemes are totally applicable for synchrotron radiation conditions.

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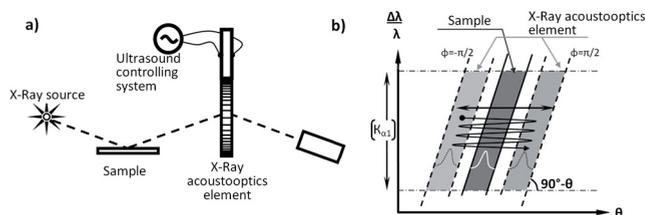


Fig.1 Experimental X-Ray optical scheme (a) and DuMond diagram (b) illustrated approach to measure rocking curves.