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Location of metals in ZnO electrospined nanofibers

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The continuous interest in ZnO based materials is caused by a promising properties which can be used in electronic and optoelectronic nanodevices. ZnO based nanostructures and particularly nanofibers are bio-safe and biocompatible. Some of their unique properties have been already successfully exploited in biological applications [1,2,3]. The most remarkable use of these oxides is found in catalysis, construction of gas sensors, and in cosmetic and pharmaceutical industries. Many properties of ZnO depends on dopants, therefore, the broad interest received ZnO based structures with metallic dopants. These dopants change the conductivity of materials from insulating to metallic, their piezoelectricity, introduce room-temperature ferromagnetism and modulate chemical sensing properties. As a result of the oxide diverse applications there is continuous searching for novel methodology to synthesize a homogeneous ZnO nanocrystals doped with metals.

The presented studies are aimed to locate Mn and Fe dopants in the ZnO nanofibers fabricated by electrospinning method. Electrospinning has been recognized as an efficient technique for the fabrication of polymer nanofibers [4]. In the electrospinning process a suspension in polymer of zinc acetate with appropriate addition of dopant metals acetates was used, followed by calcination in air, at 500°C for 4 h. The X-ray absorption method, as the element sensitive, was chosen to estimate the metal location in studied samples. The nominal content of Fe and Mn in the samples was at the level of 10 %. The electrospined thin layer of samples were deposited on the Si substrate. The K edges of Zn, Mn and Fe were measured at C and E4 stations in Hasylab, Hamburg. The Fe and Mn $L_{3,2}$ edges were measured at the I-1011 beamline at MAX-lab, Sweden. The spectra were collected in the fluorescence mode for K-edges and total electron yield for L-edges.

The electron yield technique is surface sensitive, therefore, the result of the measurements at the L-edges represent the near-surface region of the samples. The features characteristic for Mn and Fe oxides dominates in the spectra. This is consistent with the presence of nano-exclusions (20-25 nm^2) seen by scanning electron microscopy.

The Zn K-edge EXAFS spectra measured on zinc oxide nanofibers without doping confirm powder wurtzite structure typical for ZnO. In the case of the doped samples we found that around half of Zn atoms the local atomic order was changed by presence of a dopant in the second coordination sphere. From the Fe and Mn K-edges, it was established that close to 10% of all dopant atoms formed the common oxides, while about 90% of dopants substituted Zn atoms in the wurtzite ZnO structure. Such substitution introduced the local distortion of the lattice. Nevertheless, even such a small content of Mn and Fe oxides can significantly change the properties of materials, particularly magnetic ones.

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