

# Physical properties of Zn doped Fe<sub>3</sub>O<sub>4</sub> nanoparticles

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Two series of octahedral Fe<sub>3-x</sub>Zn<sub>x</sub>O<sub>4</sub> nanoparticles with mean sizes of 27 nm and 73 nm were prepared by thermal decomposition. All samples crystallize in inverse spinel cubic type structure with the Zn<sup>2+</sup> ions located in tetrahedral sites. Magnetic measurements indicate an increase of the saturation magnetizations by 20% for a Zn content of x=0.12. The estimated anisotropy constants are close to that of pure magnetite. The physical properties of the investigated series are analysed in correlation with their structural properties.

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## 1. Introduction

The applications of bio-functionalized magnetite nanoparticles for the *in vitro* diagnostic represent an important field of research due to their biocompatibility and easy removal from the body by natural routes [1]. The magnetite nanoparticles can be also efficiently stabilized in corrosive biological media, by SiO<sub>2</sub> and Au coating, ensuring plasmonic properties. However, by coating the magnetite nanoparticles with nonmagnetic shells, their magnetic moments per volume unit decrease. It is thus of interest to investigate the behaviour of magnetite-based nanoparticles where the increase of magnetization can be obtained by iron substitutions. In this context, we report the preparation and physical properties of Fe<sub>3-x</sub>Zn<sub>x</sub>O<sub>4</sub> nanoparticles that have a reduced toxicity in comparison with other ferrites [2].

The magnetite (Fe<sup>3+</sup>)<sub>A</sub>(Fe<sup>3+</sup>Fe<sup>2+</sup>)<sub>B</sub> crystallizes in a cubic inverse spinel structure, space group  $Fd\bar{3}m$ , with the lattice parameter  $a = 0.8397$  nm. The tetrahedral (A) sites are occupied by ferric ions, while in the octahedral (B) sites both ferrous and ferric ions are located. The magnetite is ferrimagnetically ordered, the iron moments in octahedral and tetrahedral sites respectively, being antiparallely oriented.

The location of Zn<sup>2+</sup> ions in the magnetite structure, as well as the magnetic properties of this system were found to depend significantly on the synthesis and/or postprocessing method [3 - 12]. Several reports suggested that a small number of Zn<sup>2+</sup> ions would occupy octahedral sites, when Fe<sub>3-x</sub>Zn<sub>x</sub>O<sub>4</sub> was prepared by coprecipitation [4], ball-milling [5, 6], twin roller grinding methods [7], sputtering [8] or pulsed laser deposition [9]. The Zn<sup>2+</sup> ions

dominantly occupy the tetrahedral sites when samples are obtained by thermal decomposition, thus inducing metastable Fe<sub>3-x</sub>Zn<sub>x</sub>O<sub>4</sub> phases with disordered arrangements of Zn<sup>2+</sup> and Fe<sup>3+</sup> ions [3, 10 - 12].

In the following, the physical properties of Zn doped magnetite nanoparticles having octahedral shapes, obtained by thermal decomposition method, are reported. The present data confirm the location of Zn<sup>2+</sup> ions in tetrahedral sites.

## 2. Experimental

### 2.1. Nanoparticles synthesis

The Zn doped nanoparticles were obtained from mixtures of 0.7 mmol iron (III) acetylacetonate Fe(acac)<sub>3</sub>, 1.05 mmol Zn (II) acetylacetonate (sample S1) or 1.0 mmol Fe (acac)<sub>3</sub>, 1.5 mmol Zn (acac)<sub>2</sub> (sample S2), with 3.78 mmol oleic acid and 52.61 mmol benzylether. The above mixtures were heated up to T = 295° C with a rate of 5° C/min, kept at this temperature 30 min and cooled down to the ambient temperature. The Zn-doped nanoparticles were magnetically separated from the mixture and washed several times with ethylic alcohol. The samples were kept in ethylic alcohol before measurements.

### 2.2. Characterization

The SPECTRO CIROSCCD spectrometer (Spectro, Kleve, Germany) was used for the determination of Fe and Zn (n=3 measurements) by ICP-OES. The samples are