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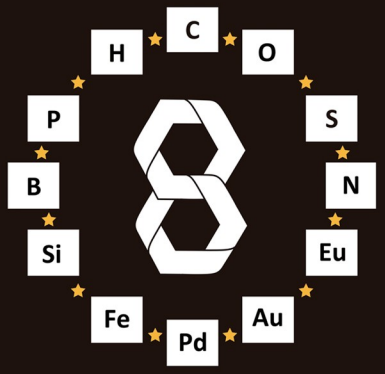
BOOK OF ABSTRACTS



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Ternary flower-structured nanoferrites with polyvalent cations for potential applications in electrochemical sensors and magnetic hyperthermia

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Nanoferrites have been intensively studied because of the possibility of their use in the fields such as medicine, sensors, environmental, agriculture, weather, battery, etc. Often, they are used as modal systems in fundamental science to study physical and chemical phenomena at the nanoscale. Various pathways were applied for the synthesis of nanoferrites with the same composition were led to different microstructure and structure properties, which further influenced magnetic, electric, catalytic and other properties. Consequently, with a controlled synthesis, it is possible to tune the properties of nanoferrites important for applications. On the other side, properties can be controlled by changing chemical composition. In ternary nanoferrites often deviation of stoichiometry accompanied with cation polyvalence was found [1]. The main idea of our work was the application of the polyol-modified method developed for the synthesis of flower-structured iron oxides nanoparticles in the preparation of ternary $Zn_xMn_yFe_zO_4$ samples to seek a correlation among chemical composition and microstructure with magnetic hyperthermia efficiency and electrochemical properties.

A series of the samples $Zn_xMn_yFe_zO_4$ was prepared by polyol process using a slightly modified procedure described in ref [2]. By elemental analysis performed using the ICP technique, the content of cations in the formula unit was determined as follow: $Zn_{0.640}Fe_{2.360}O_4$, $Zn_{0.394}Mn_{0.138}Fe_{2.468}O_4$, $Zn_{0.309}Mn_{0.240}Fe_{2.451}O_4$, $Zn_{0.182}Mn_{0.344}Fe_{2.474}O_4$, $Zn_{0.098}Mn_{0.447}Fe_{2.455}O_4$, $Mn_{0.624}Fe_{2.376}O_4$. The ICP results pointed to the presence of multivalent cations, Mn^{2+}/Mn^{3+} and Fe^{3+}/Fe^{2+}. Zn has stable valence +2, while the oxidation state of +4 for Mn couldn't be excluded. Different oxidation states of Mn and Fe and possible deviation of stoichiometry, can create physical effects [3] and make $Zn_xMn_yFe_zO_4$ suitable material in practical applications, used for modification of working electrodes in electrochemical sensors. Consequently, we have performed basic electrochemical characterisation of nanoferrites. Cyclic voltammetry of 5 mM $K_3[Fe(CN)]_6/K_4[Fe(CN)]_6$ (1:1) in 0.1 M KCl at bare SPCE and $Zn_xMn_yFe_zO_4$-modified SPCE showed that the highest peak current (I_p) was achieved using a $Zn_{0.098}Mn_{0.447}Fe_{2.455}O_4$/SPCE. The I_p was about 22% higher than the bare electrode.

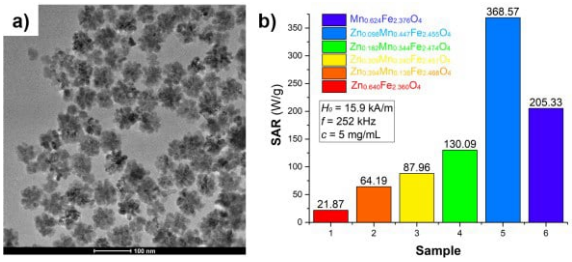

Figure 1: a) TEM micrograph of $Zn_{0.640}Fe_{2.360}O_4$, b) SAR values of $Zn_xMn_yFe_zO_4$.

X-ray diffraction pattern showed the samples were single-phase crystallising in spinel structure type. Morphology and particle size of the samples were analysed from TEM micrographs. Particles (or crystallites) were agglomerated in a flower-like structure (Figure 1). The diameter of the flowers was around 50-60 nm. Superparamagnetic behaviour of the samples was found from magnetization versus field measurements (hysteresis loops). Prepared samples were in the form of stable colloids with hydrodynamic diameter in the range of 50-120 nm. The heating properties of the samples were analysed from the data of specific absorption rate (SAR), Figure 1b. The highest SAR value was found for $Zn_{0.098}Mn_{0.447}Fe_{2.455}O_4$. The best heating efficiency and electrochemical properties had the same sample.

To correlate $Zn_xMn_yFe_zO_4$ different efficiency in magnetic hyperthermia and electrochemical sensor applications with parameters like cation distribution in two non-equivalent spinel crystallographic sites (space group, Fd-3m), local distortion on cationic sites, crystallite size and defects, an integrated study of samples structure and microstructure is in progress.

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