Magnetic properties and MCD spectroscopy of $Co_xZn_{1-x}Fe_2O_4$ nanoparticles synthesized with a citrate precursor method

*e-mail: irbiz@iph.krasn.ru

D.A. Petrov*,1, A. Thakur[2], P. Thakur[2], S.M. Zharkov[1,3], A.L. Suhachev[1], I.S. Edelman[1]

[1] Kirensky Institute of Physics, 50/38 Akademgorodok St., Krasnoyarsk 660036, Russia

[2] Amity University Haryana, Gurugram, Haryana 122413, India

[3] Siberian Federal University, 79 Svobodny Ave., Krasnoyarsk 660041, Russia

Introduction

$CoFe_2O_4$ is a hard magnetic ferrite, with moderate saturation magnetization and high coercive field [1], has a great demand in electronic industry [2]. At the same time $ZnFe_2O_4$ is a soft magnetic oxide which is chemically stable, paramagnetic in bulk and ferromagnetic in nanocrystalline form [3], plays an important role in many applications like magnetic recordings, magnetic storage. The replacement of Zn^{2+} by Co^{2+} in zinc ferrite causes changes in lattice parameter and expands range of applications of these materials. Cobalt-zinc ferrites are useful in high frequency applications due to their high value of electrical resistivity and low dielectric losses [4].

Resistivity and dielectric properties of cobalt substituted zinc ferrite of the series $Co_xZn_{1-x}Fe_2O_4$ prepared by citrate precursor technique were described in the article [3], and this work is devoted to their magnetic and magneto-optical properties.

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[3] D. Chahar, S. Taneja, P. Thakur, A. Thakur, J. Alloys Compd. 843 (2020) 155681.

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[5] Y.A. Gromova, V.G. Maslov, M.A. Baranov, R. Serrano-García, V.A. Kuznetsova, F. Purcell-Milton, Y.K. Gun'ko, A.V. Baranov, and A.V. Fedorov, J. Phys. Chem. C (2018) 11491−11497.

Magnetic properties

The field dependences of the magnetization of the samples were studied using a vibrating magnetometer VSM 8604 (LakeShore Cryotronics, USA).

Magnetization measurements were carried out for samples A–E (Fig. 1). The field dependences of magnetization indicate the ferromagnetic behavior of the samples. At room temperature the coercivity of the samples is 10–20 Oe. At T = 100 K it smoothly increases with Co content increase up to 70 Oe, for the sample D. In the sample E the coercivity reaches 220 Oe. The saturation magnetization increases by 4–5 times with decreasing temperature in samples A–D and 2.5 times in sample E. This behavior can be explained by the formation of Co nanoparticles in powders with high Co concentration.

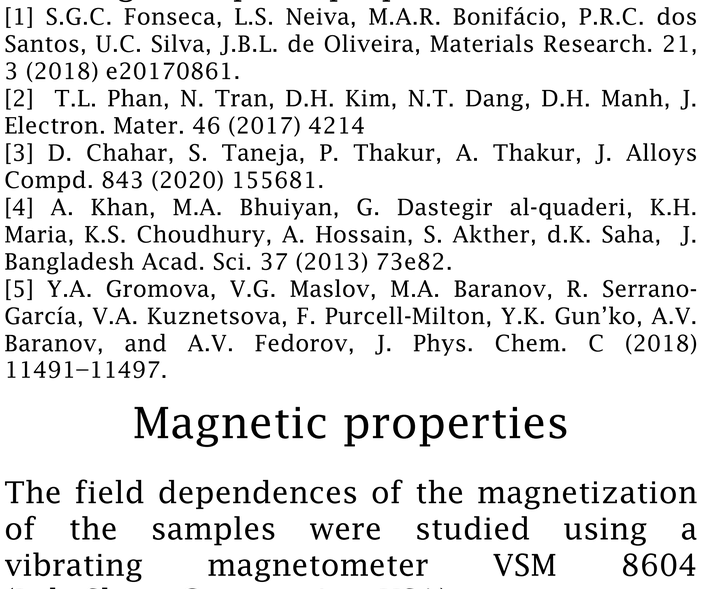

Fig. 1. *The temperature dependences of magnetization in the field 5 kOe. Insert: the field dependences of magnetization for sample E at 100 and 300 K*

Electron microscopy

The morphology, microstructure and local elemental composition of the nanoparticles were investigated using transmission electron microscopy (TEM) using a JEM-2100 (JEOL Ltd.) microscope operating at the accelerating voltage of 200 kV. The microscope was equipped with an energy dispersive spectrometer (EDS), Oxford Instruments, which was used to control the elemental composition of the samples. Selected-area electron diffraction (SAED) was used to determine the structure of NPs.

TEM images of $Co_{0.4}Zn_{0.6}Fe_2O_4$ nanoparticles is shown in fig. 2. The images for the rest of the samples look pretty much the same. Irregular nanoparticles have a size of 5–200 nm. According to analysis of ED patterns the main phase in all samples is $ZnFe_2O_4$ (Fd-3m, a=8.441 Å, PDF 4+ card #00-022-1012). HRTEM also corresponds to $ZnFe_2O_4$.

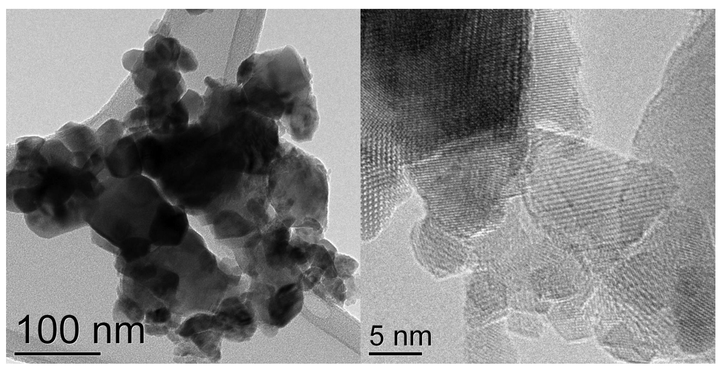

Fig. 2. *Bright-field TEM images of the sample E and HRTEM image of sample B*

The analysis of EDS data (Fig. 3) showed that the sample A is composed of $ZnFe_2O_4$, In samples B, C and D Co distributed evenly. For higher Co doses besides $Co_xZn_{1-x}Fe_2O_4$ phase were observed iron oxide nanoparticles and nanoparticles with high Co concentration.

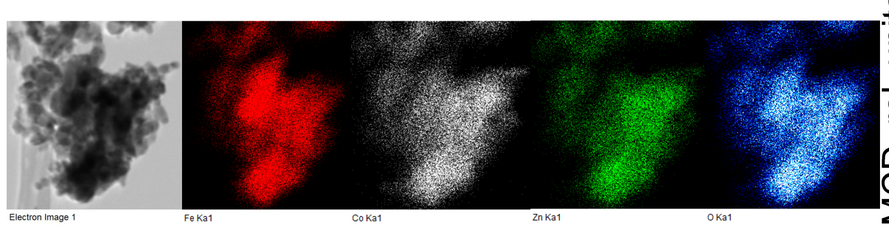

Fig. 3. *EDS data for the sample E*

Conclusions

Irregular nanoparticles have a size of 5–200 nm. No dependence of particle morphology on their composition was found. Substitution of Zn with Co leads to transition from the $ZnFe_2O_4$ phase to the $Co_xZn_{1-x}Fe_2O_4$ phase. For high doses also were observed iron oxide phase and nanoparticles with high Co concentration.

The field dependences of magnetization indicate the ferromagnetic behavior of the samples. The appearance of new phases at high Co concentration samples leads to a sharp increase in coercivity at low temperature. MCD spectra are predominantly associated with the $CoFe_2O_4$ phase.

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Magnetic circular dichroism

MCD was measured in the normal geometry. The modulation of the light wave polarization state from the right-hand to the left-hand circular polarization relatively to the magnetic field direction was used for the MCD measurements. The MCD value was measured as the difference between the sample optical density for the right and left polarized light waves.

Fig. 5 demonstrates the MCD spectra of samples D–F. For samples A and B the MCD signal slightly differs from zero. In the sample C at room temperature a noticeable signal appears near 400 nm. MCD spectra of samples D–F are in qualitative agreement with the spectra of $CoFe_2O_4$ nanoparticles in the work [5].

For samples D and E an increase in the MCD signal does not correspond to an increase in the magnetization value with decreasing temperature. This may be due to an increase in Co ions in the $ZnFe_2O_4$ sublattices or to the formation of Co nanoparticles.

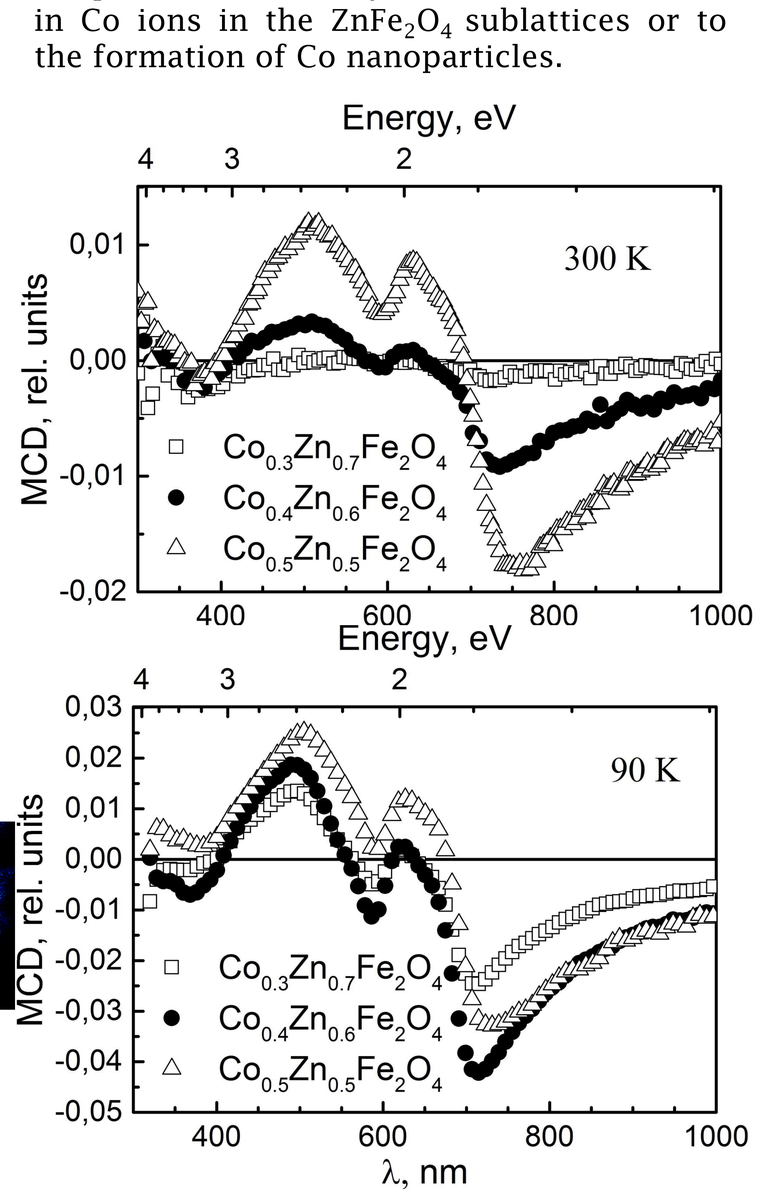

Fig. 5. *The MCD spectra for samples D-F in the field 3.5 kOe at 90 and 300 K*

Nanoparticle synthesis

Nanoparticles of $Co_xZn_{1-x}Fe_2O_4$ (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, samples A-F, correspondingly) were prepared by citrate precursor technique [1]. At first, stoichiometric amount of $Zn(NO_3)_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, and $Fe(NO_3)_3{\cdot}9H_2O$ were dissolved in 125 mL distilled water. Then 5g of citric acid was added into the solution containing metal nitrates and kept for stirring at 80 °C to get a homogeneous solid solution. After that, the samples were pre-sintered at 700 ° C for 3 h, followed by cooling to room temperature. The resultant samples were pelletized by adding 2% polyvinyl alcohol as a binder. Final sintering was done at 800 °C for 3 h.