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Large scale method to synthesize $Zn_{0.5}Ni_{0.5}Fe_2O_4$ nanoparticles with high magnetization

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Abstract. Nanostructured $Zn_{0.5}Ni_{0.5}Fe_2O_4$ ferrite is a promising magnetic material for different applications because of it good performances. In this paper, the authors present high production method for preparation of magnetic nanomaterial $Zn_{0.5}Ni_{0.5}Fe_2O_4$ - the method of spraying – co-precipitation. The advantages of this method are high productivity, good repeatability and high magnetic performances of the fabricated materials. Nanostructured $Zn_{0.5}Ni_{0.5}Fe_2O_4$ have been prepared by co-precipitation using spraying technique. Different techniques as XRD, TEM, SEM techniques were used to characterize obtained material. It is shown that prepared by this method $Zn_{0.5}Ni_{0.5}Fe_2O_4$ has face-centered cubic trevorite structure and particle size of about 15 nm. The VSM measurement has shown that obtained material is superparamagnetic with saturation magnetization (Ms) of about 60emu/g, remanences (Mr) and coercive forces (Hc) near to zero. Having so high magnetic performances, this material promises to be used for many practical applications.

Keywords. Nanoparticles,Spraying, Co-precipitation, Superparamagnetism, $Zn_{0.5}Ni_{0.5}Fe_2O_4$ ferrite.

1. Introduction

Magnetic nanomaterials find nowadays diverse technical and biomedical applications. Consequently, a wide range of novel magnetic materials, structures and process strategies are being explored [1]. For decades, the ferrite magnetic materials are the only choice for radio frequencies because it is impossible to dramatically increase resistivity of metallic magnetic materials and they were therefore excluded from high frequency applications. For this reason, efforts have been made extensively to improve the performance of the ferrites. Use of nanomaterials with different chemical composition could be perspective solution for this problem. Recently some authors have published works on synthesis of magnetic nanomaterials which are solid solutions of different ferrites [2 - 6]. It is shown, for example, that doping nickel ferrite nanoparticles with some metals can improve significantly performances of the materials. These results demonstrate the ability to control performances of the ferrite nanoparticles by chemical manipulations. In particular, the authors of [6] have studied Zn-doping effect on the energy barrier to magnetization reversal in superparamagnetic nickel ferrite nanoparticles and have showed that the materials with composition $Zn_{0.5}Ni_{0.5}Fe_2O_4$ have

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maximal magnetization which reaches 48emu/g at room temperature for applied magnetic field of 70kOe. On the other hand, for all the nano-materials, developing high-yield technology is always an actual problem.

For these reasons, we have attempted to synthesize $Zn_{0.5}Ni_{0.5}Fe_2O_4$ ferrite nanoparticles by the high production technological method: method of spraying – co-precipitation. In this paper we present results of our study on synthesis and investigation of some properties of the obtained nanoparticles.

2. Experimental

Process of synthesizing nanostructured $Zn_{0.5}Ni_{0.5}Fe_2O_4$ is shown schematically in Fig. 1. Initially, mixed liquid of $ZnCl_2$ 0.05 M + $NiCl_2$ 0.05 M + $FeCl_3$ 0.2 M is prepared with the salt $ZnCl_2$ (99%), $NiCl_2.4H_2O$ (99%) and $FeCl_3.6H_2O$ (99%) and contained in the 10*l* pressure vessel (2). The 10*l* pressure vessel (3) contains the solution NaOH 0.8 M, which is adulterated from NaOH (99%). A 3.5 atm compressed air flow shall be piped (1) into the two liquid tanks so that the liquid comes out of two pressure vessels in the mist form at the nozzles (4) and (5). Spray speeds of the two nozzles are similar and equal 0.5*l*/min. Co-precipitation reaction occurs inside 50*l* vessel (6) containing NaOH 10^{-4} M to keep the reaction environment at the constant pH = 10. Precipitate was collected, filtered and washed thoroughly until the pH reached 7÷8. The precipitated slurry was dried at temperature of 50°C, ground and then calcinated at 800°C for 4h. After calcination, the obtained powder was ground again before measurements. By the technological process described above, we have synthesized a large quantity of nanostructured $Zn_{0.5}Ni_{0.5}Fe_2O_4$ material.

The morphologies and crystal structures of the $Zn_{0.5}Ni_{0.5}Fe_2O_4$ nanoparticles were investigated by using the standart techniques of field emission scanning electron microscopy (FE-SEM, HITACHI S4800), transmission electron microscopy (TEM, JEM-100CX Instruments with an accelerating voltage of 80 kV), and X-ray diffraction (XRD, Bruker D5005 with Cu $K_{\alpha 1}$ radiation $\lambda = 1.54056$ Å). Hysteresis curves were measured using a vibrating sample magnitometer (VSM) model DMS 880 at room temperature and magnetic fields up to 13.5 kOe.

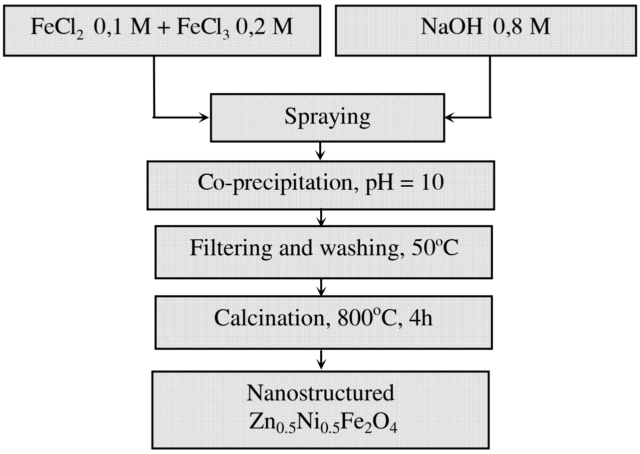
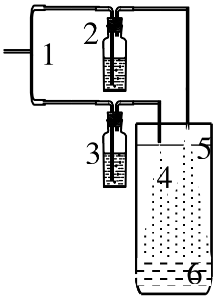


Fig 1. Schematic diagram of experimental procedure.



1 – Pneumatic tubes

2,3 – Pressure resistant vessels

4,5 – Spraying nozzles

6 – Reaction vessel

Fig 2. Co-precipitation reaction apparatus.

3. Results and disscussion

3.1 Morphology and formation of nanoparticles

The SEM image of nanoparticles is shown in Fig. 3(a). SEM image of the as-synthesized samples exhibited uniform, almost spherical shaped and loosely agglomerated particles of Ni–Zn ferrite nanoparticles, and the average particle size is about 15 nm. The TEM image (Fig. 3a) shows that the particle size is quite homogenous in the range of 8–15 nm.

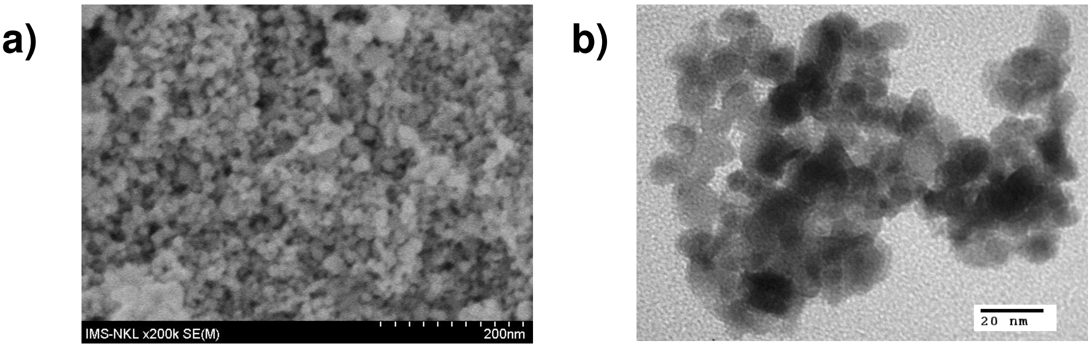


Fig. 3. SEM and TEM images of $Zn_{0.5}Ni_{0.5}Fe_2O_4$ nanoparticles (a) SEM; (b) TEM.

Fig. 4 shows the XRD patterns of the $Zn_{0.5}Ni_{0.5}Fe_2O_4$ nanoparticles. The broad and well defined difraction peaks were observed at 2θ = 18.18, 30.22, 35.48, 37.07, 43.08, 53.71, 57.05, 62.65 degrees, corresponding to (110), (220), (311), (222), (400), (422), (511) and (440) planes, respectively. X-ray diffraction data identified that the sample have face-centered cubic trevorite structure. The estimated value of lattice constants was found to be a = 8.3892Å. The value of crystallite size of the $Zn_{0.5}Ni_{0.5}Fe_2O_4$ nanoparticles was evaluated by fitting the width of (311) reflection using Scherrer formula $d = k\lambda/\beta.\cos\theta$, where k is equal 0.94, λ is the X-ray wavelength, β is the peak full width half maxima (FWHM) and θ is the diffraction peak position. The estimated value of particle size of the material is found to be about 12 nm.

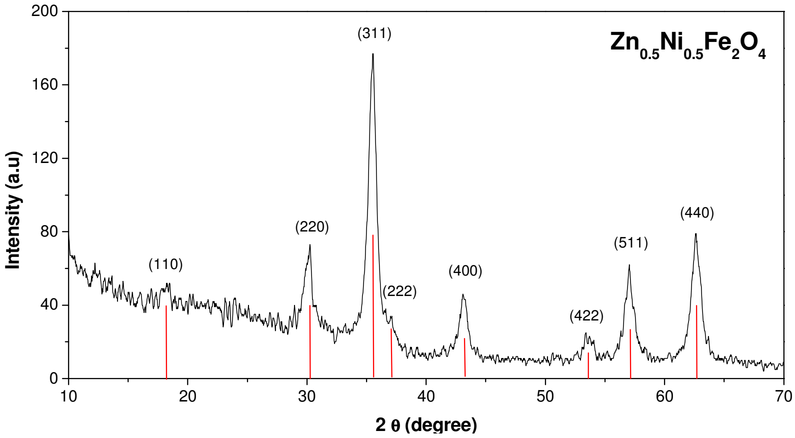


Fig. 4. XRD patterns of the $Zn_{0.5}Ni_{0.5}Fe_2O_4$ nanoparticles.

3.2 Magnetization measurement

Room temperature magnetization for compositions of $Zn_{0.5}Ni_{0.5}Fe_2O_4$ was investigated and is shown in Fig. 5. Magnetic hysteresis loops were observed in two band magnetic fields: from -1 kOe to 1 kOe (in Fig. 5(a)) and from -13.5 kOe to 13.5 kOe (in Fig. 5(b)).

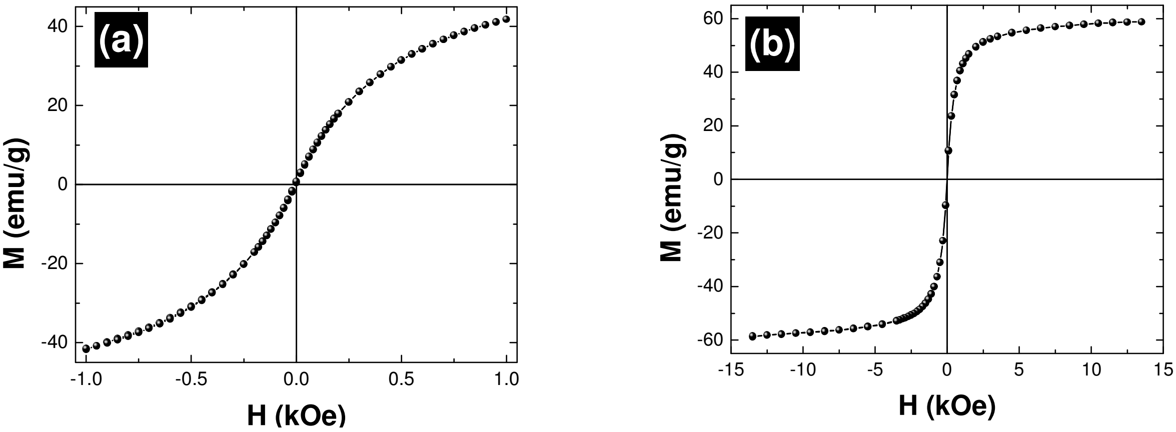


Fig. 5. Magnetic hysteresis loops of the $Zn_{0.5}Ni_{0.5}Fe_2O_4$ nanoparticles (a)in weak magnetic field; (b) in strong magnetic field

The magnetization of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles increases with external magnetic field strength, however, it does not reach the saturation state yet under a magnetic field of 13.5kOe. The VSM measurement has shown that obtained material is superparamagnetic with saturation magnetization (Ms) of about 60emu/g, remanences (Mr) and coercive forces (Hc) near to zero. More precisely, as expected for a system of magnetic nanoparticles, the magnetization does not saturate, but reaches a maximum value of about 60emu/g for the maximum applied field of 13.5 kOe. This value is much higher compared with the result that was reported in [6], where the authors have synthesized nanopartiales with composition $Zn_{0.5}Ni_{0.5}Fe_2O_4$ and get the value of saturated magnetization of 48emu/g at room temperature for applied magnetic field of 70kOe.

Using similar technological method, we obtained $NiFe_2O_4$ nanoparticles but with much less saturated magnetization (about 40emu/g at room temperature and magnetic field 13.5kOe). Thus, the introduction of zinc in the ferrite led to a marked increase in the saturated magnetization of nanoparticles. This strongly suggests that the Zn2 + ions in our Zn - Ni ferrite samples are predominantly incorporated into tetrahedral A sites. It is in good agreement with results obtained by the authors [6]. According to the study carried out in this article, with increasing content of Zn in $Zn_xNi_{1-x}Fe_2O_4$ solid solutions saturated magnetization initially increases, reaching a maximum at x = 0.5, then decreases. The authors explain this phenomenon as follows: at low content of Zn (for $x < 0.5$), saturation magnetization value increases with increasing of Zn content, because the moment of the A sublattice is gradually reduced by the incorporation of diamagnetic Zn atoms. Also, saturation magnetization value decreases for $x > 0.5$, as doping more Zn atoms into the tetrahedral sites weakens the superexchange interaction between sub-lattices A and B by reducing the Fe^{3+} occupancy in the A sublattice and by destroying the collinearity of the tetrahedral and octahedral Fe^{3+} moments.

4. Conclusion

We have developed high production method for synthesis of $Zn_{0.5}N_{0.5}Fe_2O_4$ ferrite nanomaterial: method of spraying – co-precipitation. The X-ray lines broadening, TEM and FE-SEM confirmed the nature of the nanosize particle of the powders that was 12nm and 8–15 nm, respectively. VSM measurements showed that obtained material is superparamagnetic with maximal magnetization 60emu/g at room temperature and for the maximal applied field of 13.5kOe, which is remarkably higher in comparison with reported value. Having so high magnetic performances, this material promises to be used for many practical applications.

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