Changes in the Structure and Properties of Nickel-Zinc Spinel Nanoferrites Series for 3D-Printing

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Abstract. The family of nickel-zinc nanoferrites with general formula NiₓZn₁₋ₓFe₂O₄ for 3D printing were synthesized via pyrochemical urea-nitrate method and annealed at temperatures of up to 770 K. The ferrite powder microstructure was studied by SEM and XRD methods. Average nanocrystallite sizes of 21 to 32 nm and average nanoparticles sizes of 22 to 50 nm were determined. The DC electrical conductivity of NiₓZn₁₋ₓFe₂O₄ clearly shows the change in conduction behavior of samples with increase in nickel content. The observed low electrical conductivity with values at 0.1–0.3 and 0.8–0.9 parts of nickel ion for NiₓZn₁₋ₓFe₂O₄ is due to change in cation distribution in spinel structure. The microwave absorbing properties of ferrites at 9.15 GHz were analyzed by FMR and maximum microwave absorption is that of compositions NiₓZn₁₋ₓFe₂O₄ with x = 0.15–0.30. Additive manufacturing FDM 3D-printing process with PLA-nanoferrite filament for fabricating magnetic components also was demonstrated.

1. Introduction

The nickel-zinc ferrites with general formula NiₓZn₁₋ₓFe₂O₄ are magnetic oxide semiconductors and valuable ceramic magnetic material. The nanosized nickel-zinc ferrites attract attention due to the potential of their many applications as magnetic nanomaterials, microwave absorbing materials, for protection against high frequency electromagnetic radiation and high-sensitive nanomaterials for different sensors.

Nowadays, magnetic cores and electrical conductor windings that make up magnetic components are fabricated separately in multiple, complex steps. The nanopowders of NiₓZn₁₋ₓFe₂O₄ are perspective ceramic fillers for advanced composite magnetic materials for 3D printing of machine components for mechanical engineering, machinery construction, electromechanical instruments, electromagnetic control system.

Numerous works [1–9] have presented data on the effect of substitution of nickel ions by zinc ions revealed on the electronic and electromagnetic properties of nickel-zinc nanosized ferrites. These studies show that the direct band gaps are decreased from ZnFe₂O₄ to NiFe₂O₄ [1]. Also upon an increase in the nickel content in NiₓZn₁₋ₓFe₂O₄ ferrite its magnetic properties grow and reach their maxima at nickel molar fractions of 0.5 to 0.7 [10, 11]. A further increase in nickel content reduces the magnetic properties of the nickel-zinc ferrite. Compositions of NiₓZn₁₋ₓFe₂O₄ with moderate nickel content are characterized by weak magnetic properties [3], and zinc nanoferrite at room temperature is weakly ferromagnetic [12].
or paramagnetic [10, 12, 13, 14]. The FMR resonance field decrease at the increase nickel content in Ni$_{x}$Zn$_{1-x}$Fe$_2$O$_4$ ferrite [10]. These properties can be attributed to the existence of a crystalline lattice of normal spinel in zinc nano ferrite. This type of spinel is characterized by weak interaction between its tetrahedral and octahedral sublattices and therefore has no ferrimagnetic properties. In real zinc nano ferrite samples the both types normal and inverse spinel are coexist.

The goal of this work was to investigate the effect composition of nanosized nickel-zinc ferrites with general formula Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ on the electronic and electromagnetic properties.

2. Experiment

A series of nickel-zinc spinel-type ferrites described by general formula of Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ (where $x=0$–1, with increments of 0.05) was synthesized via low temperature pyrochemical urea-nitrate processing. All reagents were weighted in stoichiometrical ratios, ground to a homogeneous paste in a porcelain mortar, and heated in porcelain crucibles from an initial temperature of 370 K with a gradual increase at a rate of about 15 K/min. After reaching 570–580 K, the reaction paste self-ignited and nitrate salts decomposed to nanosized ferrite powders. The produced raw nanoferrites powders were calcined for 30 min at 770 K for the final decomposition of nitrate salts residue and urea, and then cooled in air to ambient temperature and ground in a mortar to homogeneous powders comprised of microgranules with sizes of 2 to 5 μm. An advantage of used urea-nitrate method is the synthesis of nanosized ferrites with good magnetic properties at relatively low reaction temperatures, compared to the solid phase ceramic route sintering of powdered oxides or metal carbonates.

The crystalline microstructure of prepared Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ powders was studied via scanning electron microscopy (SEM) using a JEOL JSM 7500F microscope. The DC resistivity of nanoferrite powder samples was measured at room temperature using the two-probe method with UT-601 tester in plastic polyethylene tubes with internal diameter 2 mm and compacted ferrite powder length 5 cm under pressure contact at 1 ton/cm$^2$. The DC resistivity values were averaged from 5 measurements.

The samples of Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ specimens (where $x = 0, 0.15, 0.25, 0.5, 0.75, 0.85, 1.0$) were studied via X-ray phase analysis using a Shimadzu XRD-7000 X-ray diffractometer by using CuK$_\alpha$ radiation source with a wavelength $\lambda=1.5406\AA$ at 20 angle range from 10 to 70 with a step size of 0.02° and a count time of 1 s per step. The diffraction patterns do suggest for all the samples the presence of a unique spinel cubic phase. All the detectable peaks can be indexed to the phase of cubic spinel structure that are found as in the standard reference data (JCPDS card PDF#10-0325 for NiFe$_2$O$_4$ and PDF#89-1012 or #22-1012 for ZnFe$_2$O$_4$). The average nanocrystallite size in Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ samples were calculated using the Scherrer equation.

The UV–vis & NIR diffuse reflectance spectra of nanosized powders Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ were recorded using Hitachi U-3900 spectrophotometer with 2-channel integrating sphere at room temperature. The optical band gap can be calculated by following relation [15]:

$$ (\alpha h\nu)^k = A (h\nu - E_g) $$

(1)

where $\alpha$ is optical absorption coefficient, $A$ is constant and exponent $k$ depends on the nature of transition (for indirect band gap $k = 1/2$ and for $k = 2$ direct band gap). The optical absorption coefficient was calculated by following relation [16]:

$$ \alpha = (R_{\text{max}} - R_{\text{min}}) / (R - R_{\text{min}}) $$

(2)

where $R$ is optical diffusion reflectance.

Straight lines are obtained for both $k = 1/2$ and 2 by plotting the above equation, indicating the indirect and direct nature of band gap. The value of band gap is obtained by extrapolating the linear fitted curves of $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ to energy axis at $\alpha = 0$.

A magnetic and microwave absorption properties of the full series of powdered Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ nanoferrites was studied via FMR method using a JEOL JES FA-300 EPR spectrometer in the $X$-range at 9.15 GHz.
3. Results and discussion

According to our results all studied ferrite samples have the crystalline lattice of cubic spinel. The calculated lattice parameter systematically varied 8.351 to 8.458 Å for Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ specimens with zinc ion fraction from 0 to 1. The Zn$^{2+}$ ions have larger ionic radius (0.82 Å) than Fe$^{3+}$ (0.65 Å) and Ni$^{2+}$ (0.74 Å). For spinel ferrites the Zn$^{2+}$ ions successively replace Fe$^{3+}$ ions on tetrahedral A-site. This results in an increase of lattice parameter with the content of zinc in Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$. Average crystallite sizes as a function of nickel content were $D(x=0) = 28.8$ nm, $D(x=0.15) = 30.2$ nm, $D(x=0.25) = 29.4$ nm, $D(x=0.5) = 31.8$ nm, $D(x=0.75) = 31.4$ nm, $D(x=0.85) = 22.6$ nm, $D(x=1.0) = 21.0$ nm.

Micrographs of several prepared Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ nanoferrites are presented in figure 1.

![Figure 1. Typical SEM micrographs of Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ samples.](image)

Based on an analysis of the microimages, the estimated average ferrite nanoparticle sizes were found to range from 22 to 50 nm, depending on the ferrite composition. This result clearly reflects association of nanocrystallites in nanoparticles of prepared nickel-zinc ferrites. The minimum size of the nanoparticles was those of the Ni$_{0.75}$Zn$_{0.25}$Fe$_2$O$_4$ specimen and the maximum size of the nanoparticles was observed for Ni$_{0.25}$Zn$_{0.75}$Fe$_2$O$_4$ sample.

The UV-Vis diffuse reflectance spectra of all studied Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ samples clearly show that the Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ nanoparticles can absorb energy of photons in the wavelength range of 240 nm to 450 nm. Optical band gaps was calculated from the Tauc plot confirms the semiconducting nature of the studied nickel-zinc ferrites samples. From the figure 2 it can be seen that the calculated band gap values of the Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ samples are in the range of 1.6 eV to 2.0 eV which is comparable to the reported values [10-20]. For example the direct and indirect band gaps for our NiFe$_2$O$_4$ sample are obtained to be 1.69 eV and 1.49 eV respectively and are comparable with experimental investigations direct gap E$_g$ from 1.55 to 2.85 eV [14–22] and theoretical values of direct and indirect band gaps 2.4 and 1.6 eV [23]. The direct and indirect band gaps for our ZnFe$_2$O$_4$ sample are obtained to be 1.99 eV and 1.77 eV respectively and are comparable with experimental investigations direct gap E$_g$ from 1.66 to 2.43 eV [6, 24–27] and theoretical value 1.93 eV [28].
Figure 2. Calculated band gap, DC conductivity and FMR resonance field of the Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ samples.

DC resistivity studies are one of the useful characterization techniques to understand the conductivity mechanism in oxide semiconductors. The nature of electrical conductivity with increase in nickel content in Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ clearly shows the change in conduction behavior of the sample with different composition. The anomalous behavior of electrical conductivity with values at 0.1–0.3 and 0.8–0.9 parts of nickel ion for Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ (figure 2b) is due to change in cation distribution in cubic spinel structure.

The FMR resonance field of Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ ferrite versus composition (Figure 2c) decrease with the nickel content grows from 0 to 0.5, then increase at nickel fraction >0.5 up to 0.85 and also decreased at nickel fraction >0.85 in Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$. The results from FMR spectroscopy demonstrate the strong dependence of magnetic and microwave absorption properties on the composition of the considered nickel-zinc ferrites. Upon an increase in the nickel content in ferrites, the values of the magnetic resonance field diminishes, indicating a resonance shift to lower frequencies. The absorption line width also varies at different fractions of nickel in Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$. The magnetic field absorption line width sharply increased e with the nickel content grows from 0 to 0.2, then approximately constant in 0.2–0.5 nickel part range, also increase at nickel fraction >0.5 up to 0.6 and also decreased at nickel fraction >0.6 in Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$. Thus, the maximum absorption line width of synthesized nickel-zinc nanoferrites range is belong to compositions with molar fractions of nickel $x = 0.20–0.65$. So, we can see that the composition of nanosized nickel-zinc ferrite greatly affects its magnetic and microwave absorption properties. Compositions of Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ ferrite with approximately equal contents of nickel and zinc ions are characterized by the lowest FMR resonance field (Figure 2c). Also was found that the maximum microwave absorption properties of synthesized nickel-zinc nanoferrites that calculated via integral of FMR absorption line normaliz e to sample mass is achieved at unexpectedly minor content of nickel ions in the ferrite at the $x = 0.15–0.30$ range. The obtained in this study microwave electromagnetic properties of nickel-zinc ferrites are in good agreement with the previous FMR studies of nickel-zinc nanoferrites [29].

Additive manufacturing FDM 3D-printing process with for fabricating magnetic components also was studied in this work. The ferrite fraction in plastic for 3D printing is desired to be as high as possible to provide the highest magnetic permeability for across a printed component. However, the ferrite fraction in plastic must be low enough so as to enable the material to exit the heated extrusion nozzle of the 3D printer. Polylactide (PLA) polymer filament (FDplast, Russia) which is a readily available modeling plastic was chosen as the matrix polymer in our investigation due to its well-known ease of printing, low cost and wide availability. We carried out optimization between composite filament extrusion production, printing parameters, and reliable operation, the maximum fraction is 35% weight ferrite. We make note that at higher ferrite nanopowder fractions the filament tends towards brittle behavior in feeding and becomes difficult to print. The printability of the composite filament was assessed by printing simple blocks using the FDM process. The composite filament is driven by a stepper motor into a temperature controlled nozzle and molten material is extruded and deposited onto the build platform in a layer according to the pre-programmed pattern. Figure 3 shows printed blocks of pure PLAABS and PLA + 35 weight ferrite of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ and results of complex dielectric permittivity and magnetic permeability measurement.
Figure 3. Photographs of printed PLA (top) and PLA + 35 weight of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ (bottom) blocks and frequency dispersions of complex permittivity and permeability for printed PLA + 35 weight of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$

4. Conclusions
The full series of nickel-zinc ferrites with general formula Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ (where $x = 0$–1) were synthesized and annealed at temperatures of up to 770 K. The prepared ferrite powder crystal structure and microstructure was studied using SEM and XRD. Average nanocrystallite sizes of 21 to 32 nm were determined according to XRD, while average nanoparticle sizes of 22 to 50 nm were determined according to SEM micrograph analysis. The optical diffuse reflectance measurements were carried out at room temperature gives the values of calculated band gap for the Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ samples are in the range of 1.6 eV to 2.0 eV. The DC electrical conductivity of Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ shows the change of cation distribution in cubic spinel structure with increase in nickel ion content. The FMR resonance field of Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ ferrite samples versus composition decrease in the nickel content grows from 0 to 0.5 and increase at nickel fraction $>0.5$ up to 0.85 in Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$. The maximum absorption line width is that of compositions with molar fractions of nickel $x = 0.20$–0.65. It was found that the maximum microwave absorption of Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ nanoferrites in high-frequency electromagnetic wave range is achieved at minor content of nickel ions in the ferrite in the $x = 0.15$–0.30 range.

Additive manufacturing FDM 3D-printing process with PLA-nanoferrite filament for fabricating magnetic components also was demonstrated.

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