

2-2005

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Recommended Citation

Vuk Uskoković, Miha Drogenik. (2005). Synthesis of relatively highly magnetic nano-sized NiZn-ferrite in microemulsion at 45 oC. *Surface Review and Letters* 12:01.
doi: 10.1142/S0218625X05006822

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This is a pre-copy-editing, author-produced PDF of an article accepted for publication in *Surface Review and Letters*, volume 12, issue 1, in 2005 following peer review. The definitive publisher-authenticated version is available online at DOI: [10.1142/S0218625X05006822](https://doi.org/10.1142/S0218625X05006822).

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Synthesis of Relatively Highly Magnetic Nano-Sized NiZn-Ferrite in Microemulsion at 45 °C

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Abstract

The procedure for the preparation of NiZn-ferrite powder with average particle size of 10 nm and saturation magnetization of 50 emu/g by using precipitation reaction between acidified sulphate precursor salts and NH₄OH as the precipitating agent in the water-in-oil domain of the microemulsion CTAB/1-hexanol/water at 45 °C is presented herein. TEM measurements have revealed relatively uniform morphology of the particles, which are associated in coral-like agglomerates. EDS measurements have been used for qualitative analysis of the sample, whereby FAAS measurement has been performed in order to reveal the proportion of the cations in the sample - Ni : Zn : Fe = 0.17 : 0.18 : 2.64.

Introduction

NiZn-ferrites are irreplaceable magnetic ceramics for the contemporary electronic industry, primarily due to their high electrical resistivities that imply low eddy current losses [1]. These properties provide NiZn-ferrites large utilization within high-frequency (10-500 MHz) applications, such as radio-frequency circuits, high-quality filters, rod antennas, miniaturized transformer cores, high-frequency inductors, high-speed digital recording heads, microwave devices etc. Due to the direct dependence of resistivity and inverse dependence of eddy current losses on the concentration of grain boundaries, the production of nano-sized NiZn-ferrites with sufficient magnetization values presents a noteworthy challenge.

The wet approaches to the synthesis of materials offer many advantages comparing to the traditional method of high-temperature processing, including better control of the final powders' stoichiometries with possibilities of obtaining homogeneity and mixing on atomic scale, narrow particle sizes distribution, negligible contamination of the product during the homogenization of the starting compounds, low energy consumption (especially if high-T treatment can be completely avoided as in the case presented herein), low aging times and simple equipment. Microemulsion-assisted preparation of materials might have additional qualities, due to the wide range of possible interactions for different microemulsion compositions, having unique influence on the particle formation processes.

Experimental

A single-microemulsion approach was followed within the procedure for the synthesis of nanosized NiZn-ferrite particles. 12 g of CTAB (>99%, *Alfa Aesar*) as surfactant, 27.5 ml of 1-hexanol (>98%, *Merck-Schuchardt*) and 7 ml of the aqueous solution comprising 0.237-M overall concentration of cations – Fe²⁺, Zn²⁺ and Ni²⁺

(molar ratio of Fe : Zn : Ni = 4 : 1 : 1) as sulphates ($FeSO_4 \times 7H_2O$ (>99%, Alfa Aesar), $NiSO_4 \times 7H_2O$ (99.7%, Podnart) and $ZnSO_4 \times 7H_2O$ (>99%, Alfa Aesar)), were successively poured into a vessel and stirred until translucent solution was obtained. The composition of the microemulsion was CTAB : hexanol : water = 29 : 54 : 17 in weight proportion, which belongs to the reverse micellar region in the corresponding phase diagram [2]. The precursor solution of cations was acidified by the addition of 1-M aqueous solution of H_2SO_4 (99.8 %, Carlo Erba) to pH = 1.6 (2.75 %v/v) in order to hinder the oxidation of dissolved Fe^{2+} ions. pH of the resulting microemulsion was 2.2. The temperature was kept at 45 °C during the whole course of the experiment. Magnetic stirrer was used to agitate the microemulsion mixture throughout the whole course of the experiment. 18 ml of the 25 % NH_4OH (Merck) standard aqueous solution was then added into the microemulsion in order to initiate the precipitation of precursor cations in form of hydroxides. The composition of the microemulsion with the addition of NH_4OH changed to CTAB : hexanol : water = 20.2 : 37.7 : 42.1, which belongs to the phase diagram region where highly-percolated reverse micellar and two-phase regions are colligated [2]. pH at the beginning of the precipitation was 11 and gradually fell to 10.3 after 15 min and 10 after 30 min of the aging time. Thirty minutes after the initiation of the precipitation reaction, 1.5 ml of the standard aqueous solution of H_2O_2 (30 wt%, Carlo Erba) was added into the reaction vessel. pH continued to decrease, to 9.6 at the 45th minute of the aging time, and to pH = 8.9 at 50th minute of the aging time. After 1.5 h aging time, sedimentation of the solid phase was induced by centrifugation (Eppendorf Centrifuge 5804) at 3500 rpm for 3 min. The resulting brown powder was washed repeatedly with ethanol (99.8 %, Carlo Erba) and distilled water, alternately, in order to eliminate remaining surfactant and oil-phase molecules. The powder was then dried at 60 °C in air.

The dried powder was analyzed by using TEM (JEOL JEM-2000FX), magnetic measurements (Manics DSM10) and X-ray diffraction analysis (D4 Endeavor). Average particle sizes were estimated by using Debye-Scherrer's equation on the (311) diffraction peak of the spinel products. The samples for TEM analysis were dispersed in ethanol with the aid of ultrasound, and then applied to a copper grid, where they were allowed to dry and were later viewed on TEM. The stoichiometry of the synthesized powder was determined by flame atomic absorption spectrometry (FAAS), using a Varian Spectra AA 110 instrument, in an air-acetylene flame.

Results and discussion

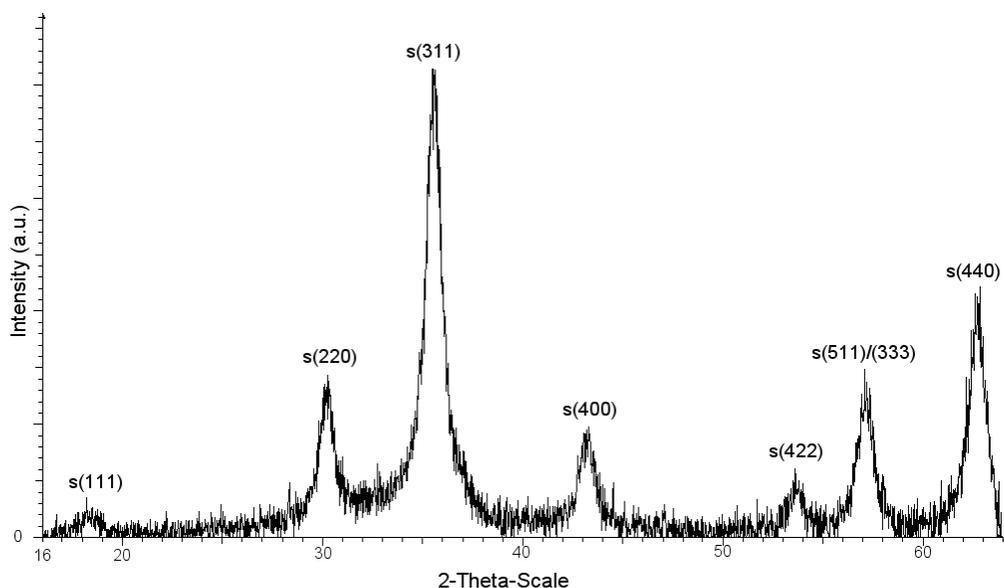


Fig. 1. XRD pattern of the NiZn-ferrite synthesized in CTAB/1-hexanol/water microemulsion at 45 °C. Peaks denoted with S belong to the spinel crystalline phase of the ferrite sample.

XRD pattern of the synthesized sample is shown in Fig. 1. The average particle size is, according to the Debye-Scherrer's equation, equal to 10 nm. Since theoretical calculations have yielded an estimated lower limit on the critical crystallite dimensions of NiZn-ferrite at ~ 21 nm under which the particles are single-domained [3], the particles synthesized within the presented experiments might be taken as single-domained as well.

TEM images of the synthesized powder captured at different magnifications are shown in Fig. 2. The powder consists of agglomerated particles of low polydispersity in size. The agglomeration of the powder prevents limiting of superexchange interaction to individual, single-domain magnetic particles and exhibiting superparamagnetic behavior. The size of the particles as observed by TEM is consistent with the average particle size of 10 nm as estimated from XRD measurements by using Debye-Scherrer's equation.

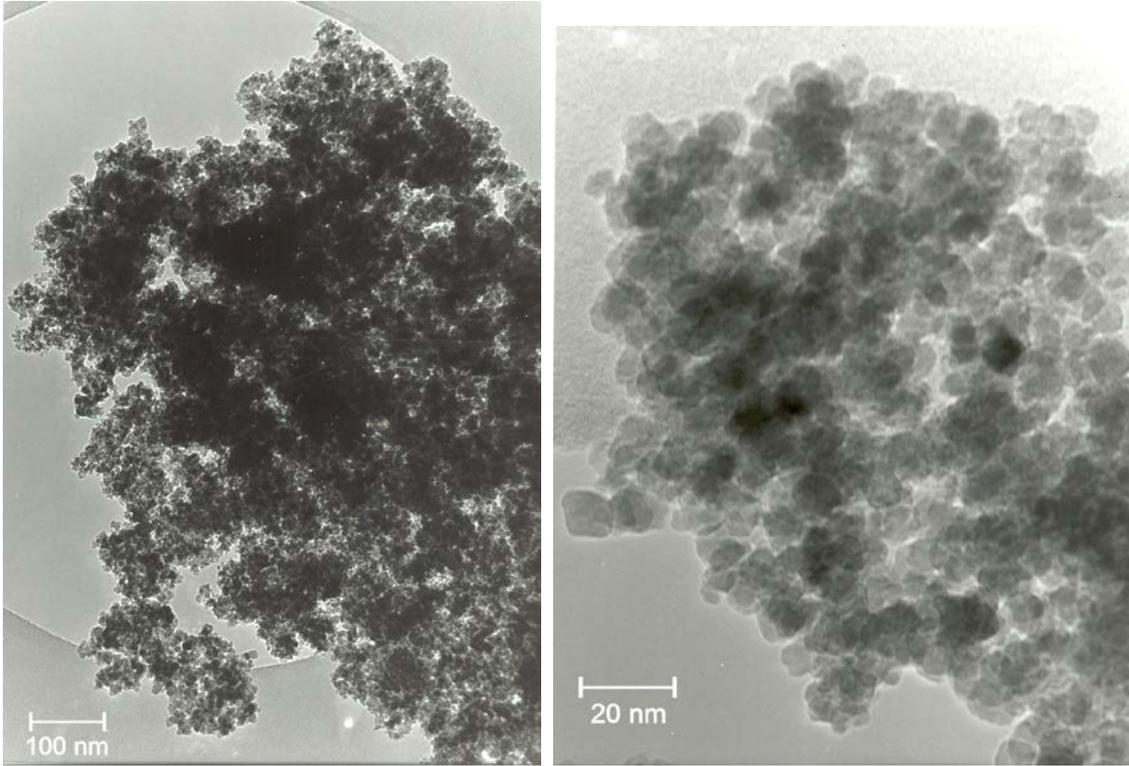


Fig. 2. TEM images of the synthesized powder at different magnifications.

Saturation magnetization of the synthesized sample is $M_s = 50$ emu/g, which is more than a half of the magnetization which high-temperature processed and sintered samples of the same chemical composition usually exhibit [4]. Remanence magnetization $M_r = 1.9$ emu/g, whereby coercivity $H_c = 32$ Oe. Hysteresis loop of the synthesized sample is shown in Fig 3.

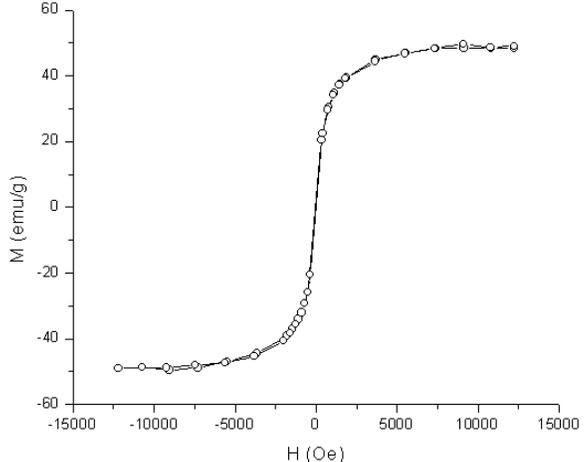


Fig. 3. Hysteresis loop of the synthesized NiZn-ferrite.

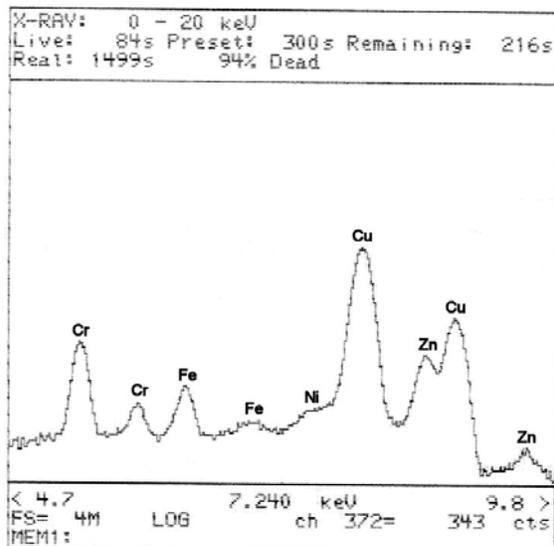


Fig. 4. EDS spectrum of the synthesized NiZn-ferrite.

EDS spectrum of the synthesized NiZn-ferrite is shown in Fig. 4. The peaks corresponding to all three constituent cations of the synthesized magnetic material are visible, together with peaks corresponding to Cu and Cr, deriving from the grid used as a powder carrier within the given analysis.

The ideal nickel-zinc ferrite has the molar ratio of $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$. However, FAAS results for the herein synthesized material, normalized to the ferrite notation are 0.17 : 0.18 : 2.64, which indicates that more than half of nickel and zinc ions were lost in the synthesis. Morrison et al. [4] have by using EXAFS analysis revealed that NiZn-ferrite with a similar stoichiometry ($\text{Ni}_{0.20}\text{Zn}_{0.44}\text{Fe}_{2.36}\text{O}_4$), synthesized by an AOT-based reverse micelle method at room temperature, possesses two-layered structure with unevenly distributed cations within the particles.

Performed variations of the presented procedure of synthesis did not yield material with desired magnetic properties. Exclusion of Ni^{2+} and Zn^{2+} precursor salts resulted in obtaining spinel product (magnetite) with $M_s = 15$ emu/g, whereas performing the synthesis at room temperature resulted in the formation of amorphous product, with lower magnetization by an order of magnitude. The viability of the performed procedure in relation to the production of relatively highly-magnetic and uniform, 10 nm-sized particles of NiZn-ferrite might lie in the specific structure of the parent microemulsion of the synthesized powder. Because a single-microemulsion approach was used within the synthesis procedure presented herein, the composition of the microemulsion changed after the addition of each of the two reagents - precipitating and oxidizing agents. Due to the increase in water percentage of the microemulsion, the reverse micelles grew in size until the complex surfactant assemblies transformed to bicontinuous, highly-percolated aqueous channels, which obviously permitted advantageous grain growth with significant effects on the magnetic properties of the synthesized powder.

Conclusions

The procedure for the synthesis of NiZn-ferrite particles by using CTAB/1-hexanol/water microemulsion is presented. The saturation magnetization of the particles is 50 emu/g, which is approximately a half smaller when compared to the traditionally synthesized NiZn-ferrites. However, relatively short aging time of 1.5 h, low aging temperature of 45 °C as well as the simplicity of the equipment used are obvious advantages of the presented method. By performing FAAS analysis it was revealed that the proportion of cations in the synthesized sample is: Ni : Zn : Fe = 0.17 : 0.18 : 2.64, which is a sign that more than half of the precursor nickel and zinc ions were lost during the synthesis. Agglomerated nature of the synthesized particles and low dispersity in size were evidenced by using TEM.

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