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SYNTHESIS OF NANOCRYSTALLINE NICKEL-ZINC FERRITES WITHIN REVERSE MICELLES

SINTEZA NANOKRISTALINIČNIH NIKELJ-CINKOVIH FERITOV V REVERZNIH MICELAH

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Nanocrystalline nickel-zinc ferrites were synthesized via a reverse micelle microemulsion route. The precursor cations were precipitated in the microemulsion system CTAB/1-hexanol/water. A subsequent oxidizing reaction was used to synthesize the nickel-zinc ferrite. The obtained nanoparticles were less than 20 nm in size.

Keywords: nanomaterials, ferrite, powders synthesis, microemulsion, reverse micelle

Nanokristalinične nikelj-cinkove ferite smo sintetizirali z reverzno mikroemulzijsko metodo. Prekurzorski kationi so bili precipitirani v mikroemulzijskem sistemu CTAB/1-heksanol/voda, z naslednjo reakcijo oksidacije pa je bil dobljen nikelj-cinkov ferit. Velikost sintetiziranih nanodelcev je bila manjša od 20 nm.

Ključne besede: nanomateriali, ferit, sinteza prahov, mikroemulzija, reverzne micele

1 INTRODUCTION

The reverse micelle synthesis of ferrite nanocrystallites has recently been shown to be a very promising method for obtaining ultrafine (superpara)magnetic particles with a number of actual and potential fields of application[1-3].

The microemulsion technique is an excellent method for the preparation of nanosized magnetic powders since the morphology of the particles, uniform in terms of size and shape, can be effectively designed by changing the composition of the water-in-oil microemulsions in the applied phase diagram. The presence of water is important since it is able to vary the size of the surfactant aggregates, or so-called »water pool«, characterized by water-to-surfactant molar ratio (parameter w).

In the process of synthesizing ultrafine ferrite materials within reverse micelles there are many parameters that influence the synthesized-powder morphology and stoichiometry, and hence its properties and applicability. In this study we limited our investigation to the influence of different proportions of the components of the system on the morphology and magnetization of the prepared ferrite nano powders.

2 EXPERIMENTAL PROCEDURE

For the microemulsion system we used a three-component system consisting of hexadecyl trimethyl ammonium bromide (CTAB) as a surfactant, 1-hexanol as an oil phase and water as an aqueous phase[4]. In order to obtain the right composition, which would form reverse micelles, the composition of the water-in-oil microemulsions was modified.

Microemulsions were formed at temperatures around 45 °C with well-defined amounts of solutions of ferro- (1 M), nickel- (0,25 M) and zinc- (0,25 M) sulphates in deionized water encapsulated in water pools of the microemulsion in proportions to match the desired ferrite stoichiometry, which was $Ni_{0,5}Zn_{0,5}Fe_2O_4$. A solution of NaOH was used as a precipitating agent.

The precipitated samples were left to age for half an hour. After that time, hydrogen peroxide was added to the mixture, and at this stage the process of forming the spinel crystal structure of nickel-zinc ferrite was initiated. The co-precipitation synthesis of nickel-zinc ferrite, which takes place within the reverse micellar structures, can be described with the following chemical reaction:

$$xNi^{2+} + yZn^{2+} + (3\text{-}x\text{-}y)Fe^{2+} + 6OH^- + \frac{1}{2}O_2 \rightarrow$$
$$\rightarrow Ni_xZn_yFe_{3\text{-}x\text{-}y}O_4 + 3H_2O$$

and in our experiments, x + y was set to be 1.

Analytical meaurements were performed in order to detect possible leaching of Zn^{2+} ions. The magnetization of the samples was determined using the Manics DSM10 suscepto-magnetometer. Specific surface-area measurements were performed with a Micromeritics Gemini II surface-area analyzer by using the multi-point BET method. With the Debye-Scherrer equation and the (311) X-ray diffraction line broadening, we obtained average particle sizes. TEM observations were performed in

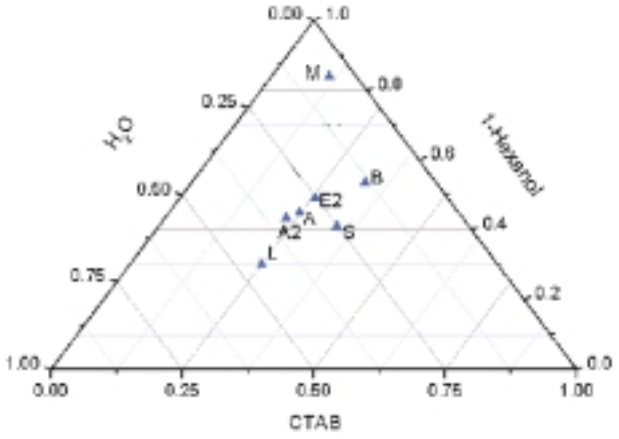

Figure 1: Composition diagram of CTAB/1-hexanol/water micro-emulsion system with the synthesized samples labelled on the diagram
Slika 1: Fazni diagram mikroemulzijskega sistema CTAB/1-heksanol/voda z označenimi sintetiziranimi vzorci

order to examine the morphology of the powders at the nanometer level.

3 RESULTS AND DISCUSSION

Figure 1 shows the positions of the synthesized samples (denoted as L, S...) in the phase diagram, and according to the reports of Ekwall *et al.*[5], all the samples fall into the region of reverse micelles.

Both the CTAB/1-hexanol and H_2O/CTAB ratios (the latter described by the parameter w = [H_2O] / [S], where brackets indicate concentrations) were varied, which caused the average size of the grains formed with the assistance of the reverse micelles to change as well.

A characteristic XRD pattern of a representative sample is shown in **Figure 2**. The powder is crystalline, with an average grain size of the ferrite particles of around 10 nm.

Table 1 shows the calculated average particle sizes from specific surface-area measurements as well as from the X-ray diffraction broadening of line (311), together with the saturation magnetization of the samples at room temperature, parameter w and the CTAB/hexanol weight ratio. Our results indicate that the synthesis of the nanosized nickel-zinc ferrite at different points in the phase diagram, shown in Figure 1, yields products which differ in terms of their average grain size and magnetization.

Table 1: Molar ratio of water to CTAB (w), CTAB/hexanol weight ratio (α), specific surface area of the sample (A_S), average particle size estimated from the samples' specific surface areas (d_A), average particle size estimated from the broadening of the (311) X-ray diffraction peak (d_x) and room-temperature saturation magnetization (σ_s)
Tabela 1: Molsko razmerje voda/CTAB (w), masno razmerje CTAB/heksanol (α), specifična površina vzorcev (A_S), povprečna velikost delcev, ocenjena iz specifične površine vzorcev (d_A), povprečna velikost delcev, ocenjena iz širine (311) difrakcijskega vrha (d_x) in nasičena magnetizacija pri sobni temperaturi (σ_s)

Sample	w	α	A_S (m^2/g)	d_A (nm)	d_x (nm)	σ_s (emu/g)
L	36,44	0,833	65	19,4	9,9	13.8
A2	29,57	0,527	90	13,9	12,9	21,1
A	24,63	0,552	172	7,3	10,1	27,3
E2	19,66	0,525	119	10,5	8,5	17,0
S	14,91	0,829	106	11,8	8,2	20,4
M	9,20	0,131	130	9,6	5,8	8,3
B	8,28	0,617	/	/	/	5,0

As can be seen from **Table 1**, the average particle size is in the range of 5.8 to 12.9 nm, while the saturation magnetization at room temperature is between 5 and 27.3 emu/g. The average particle sizes obtained from the specific surface-area measurements have, in most cases, greater values than the same quantity obtained from the X-ray diffraction measurements, which suggests that the final powders are agglomerated.

Ferrites with such a small average particle size are expected to exhibit superparamagnetic behaviour. Nevertheless, the measured coercivities of samples A and E2 at room temperature gave us values of 25,4 Oe and 24,8 Oe, respectively, which is an obvious sign that

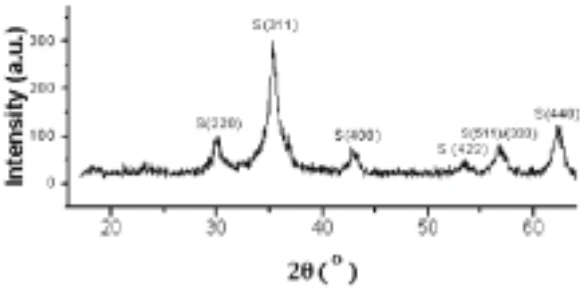

Figure2: X-ray diffractogram of the sample S. The peaks denoted with S stand for spinel crystal structure of nickel-zinc ferrite
Slika 2: Rentgenski difraktogram vzorca S. Vrhovi, označeni z S, pomenijo spinelno kristalno strukturo nikelj-cinkovih feritov

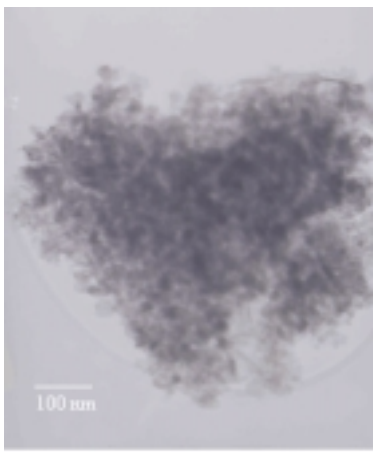

Figure 3: A TEM image of a typical nano powder, synthesized using a reverse micellar microemulsion mixture
Slika 3: TEM-mikrograf tipičnega nanoprahu, sintetiziranega z reverzno mikroemulzijsko zmesjo

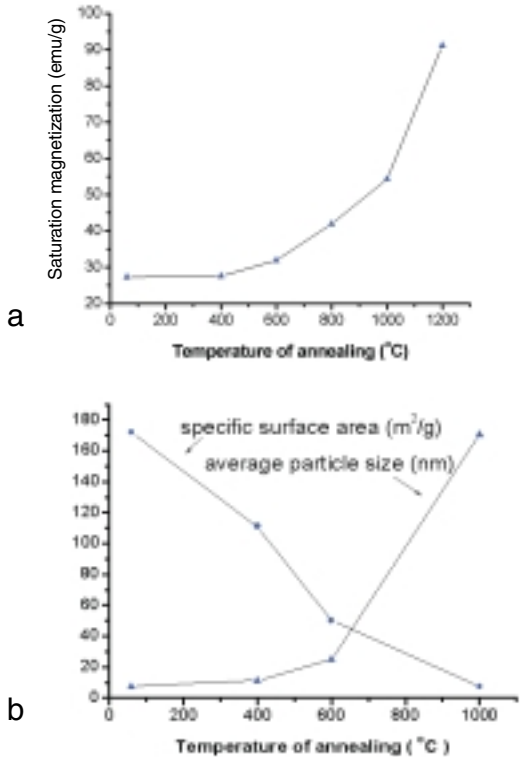

Figure 4: Saturation magnetization (a) and the average particle size (b) versus temperature of annealing for 2 hours in air

Sliki 4: Nasičena magnetizacija (a) in povprečna velikost delcev (b) kot funkcija temperature segrevanja dve uri na zraku

agglomeration, to a certain extent, occurred within those samples during their syntheses.

Figure 3 shows us a typical electron micrograph of sample A, which was synthesized within reverse micelles. We can see that the sample consists of very fine particles that are about 10 nm in size. These observations are consistent with the average particle size obtained from the specific surface measurements (9.6 nm), while the average particle size obtained from the broadening of the (311) diffraction line is 5.8 nm. The tendency of the powder to agglomerate is also obvious. Even though the synthesized magnetic particles are single domain in nature, the exchange interaction is not limited to individual particles and so the whole agglomerate in **Figure 3** behaves as one giant magnetic particle showing no superparamagnetic behaviour, which was evidenced by the very large values of coercivity, typical for agglomerated magnetic nanosystems[6].

After annealing sample A in air at different temperatures for two hours, an increase in the values of the saturation magnetization was observed (**Figure 4a**): from about 27 emu/g, for the as-dried powder, a very slight increase for the sample heated at 400 °C, and then the saturation magnetization jumped to more than 90 emu/g for the sample which was heated at 1200 °C. A rearrangement of the magnetically disordered surface of the particles and a refinement of the crystal structure obviously led to a better superexchange interaction between the magnetic moments of individual ions and thus to a higher saturation magnetization.

On the other hand, the heating of sample A at different temperatures caused a decrease in the specific surface, which was induced by the growth of bigger grains as a result of the disappearance of the smaller ones. The dependence of the average grain size, as calculated from the measured specific surface area, on the temperature of the annealing is shown in **Figure 4b**.

4 CONCLUSION

Nickel-zinc ferrites synthesized via a reverse micelle microemulsion were nanosized. The properties of the powders changed significantly, depending on the composition of the microemulsion system. We found that together with varying the size of the reverse micelles described by the parameter w and weight proportion between the three basic components of the microemulsion mixture, various essential properties of the nanoferrite powders including average particle size, morphology, specific surface area, crystallization degree and saturation magnetization change as well.

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