Synthesis of nanocrystalline nickel-zinc ferrites under hydrothermal conditions

Bulat R. Churagulov, Alexander A. Burukhin, Nikolai N. Oleynikov, Pavel E. Meskin
Inorganic Chemistry Division, Chemistry Department, Moscow State University
119899, Leninskie Gory, Moscow, Russia

The synthesis of nanocrystalline powders was undertaken for zinc ferrite $ZnFe_2O_4$, nickel ferrite $NiFe_2O_4$, nickel-zinc ferrite (with composition $Ni_{0,2}Zn_{0,8}Fe_2O_4$ $Ni_{0,5}Zn_{0,5}Fe_2O_4$) as well as for simple oxides of iron (III), zinc and nickel. The synthesis was carried out under hydrothermal conditions (temperature range 130-250°C, time of treatment 1-6 hours) after preliminary precipitation amorphous metal hydroxides by ammonia (up to pH=6-9) from aqueous solutions of the corresponding nitrates. Thus obtained powders were studied X-ray diffraction, thermogravimetric analysis, scanning and transmission electron microscopy. Specific magnetic susceptibility χ was determined for the obtained samples of ferrites at the temperature range 20-298K.

1. Introduction

During the last decade the methods of soft chemistry which involve the treatment of aqueous solutions at high pressure and subcritical as well as supercritical temperatures are widely used for the synthesis of nanosized oxide powders[1,2].

The purpose of this work is a synthesis of nanocrystalline zinc $ZnFe_2O_4$, nickel $NiFe_2O_4$ and nickel-zinc $Ni_xZn_{1-x}Fe_2O_4$ ferrites powders under mild hydrothermal conditions (130-250°C) and study the influence of synthesis conditions (pH, temperature, time of treatment) on ferrite properties (composition, morphology, magnetic properties). The synthesis of simple oxides of iron, zinc and nickel was also investigated.

2. Experimental

Nitrates of iron (III), zinc and nickel ($Fe(NO_3)_3*9H_2O$; $Zn(NO_3)_2*6H_2O$ and $Ni(NO_3)_2*6H_2O$ reagent grade) in stoichiometric ratio were used for preparation of 0.5M starting solution for ferrite synthesis. Concentrations were determined by EDTA titration. In the case or simple oxide preparation concentrations were 0.5M for Ni^{2+}, Zn^{2+} and 0.25M for Fe^{3+}. Then the starting solutions were hydrolyzed up to specified pH (6-9) by dropwise addition of 2.7M ammonia under vigorous stirring. Hydrothermal synthesis of ultrafine oxide powders was performed in 50 ml Teflon lined autoclave at temperatures from 130 to 250°C. The time of treatment was varied from 1 to 6 hours. After the synthesis, the product was filtered and washed by distilled water and then dried at 80°C. Actual cation composition of prepared ferrites was refined by mother liquor analysis using polarography [3] and EDTA titration.

X-ray diffraction (XRD) analysis was performed at DRON-3M diffractometer (Cu k_α radiation). Particle size was determined by XRD peak broadening effect [4] and transmission (TEM) as well as scanning (SEM) electron microscopy (JEOL JEM FX2000II). Thermogravimetric (TG) and differential thermal analyses (DTA) were realized by Ulvac thermoanalyser (Sinku-Riko). Specific magnetic susceptibility of prepared ferrites at temperature range 20-298 K was measured in alternating magnetic field at APD Cryogenics apparatus.

3. Results and discussions

Simple oxides. The morphology of prepared simple iron, zinc and nickel oxides are presented at Fig.1. Iron oxide was synthesized from iron hydroxide gel, precipitated at pH=11. As a result of hydrothermal treatment at 250°C for τ=6 hours ultrafine α-Fe_2O_3 (mean crystallite size 75 nm by TEM, Fig.1a) was obtained.

Well crystallized zinc oxide was prepared at t=250°C, τ=6h, pH=7. According to SEM images (Fig.1b) the particles are rod-like of 5-7×1-1.5μm. The particle size of zinc oxide is almost independent of temperature (130-250°C) and time of treatment (1-6 hours). The similar phenomenon was observed in [5]. However, the particle shape of prepared zinc oxide is noticeably different from that one prepared in [5]. The rod-like particles in [5] was observed only at pH>11.

Nickel oxide, prepared at t=250°C, τ=6h, pH=9 is crystallized as plate-like particles 200-500 nm in width. Crystallite size of iron, zinc and nickel oxides particles, prepared at 230°C and treatment time 6 hours, is summarized in Table 1.

Table 1. Crystallite size of nanocrystalline ferrites prepared under hydrothermal conditions.

Sample	Average size, nm	
	Determined by XRD	Determined by SEM and TEM (*)
α-Fe_2O_3	55-65	55-75*
ZnO	-	1500x6000
NiO	-	200-500

Hence the hydrothermal synthesis under similiar conditions of iron (III), zinc and nickel oxides leads to the formation of powders with the size difference of about two orders of magnitude (Figs.1a, 1b, 1c, Table 1). Undoubtedly this fact is related to the difference in chemical nature of the oxides obtained.

Ferrites. In the case of zinc ferrite during the precipitation of amorphous zinc hydroxide gel the pH was thoroughly controlled. It is known that the zinc hydroxide possesses a amphoteric character that is why the pH equal to 8 was maintained according to [6]. For a more basic or acidic media the precipitation was not

complete and the gel precipitated at 7 ≥pH ≥ 9.0 contained hematite as impurity according to XRD data.

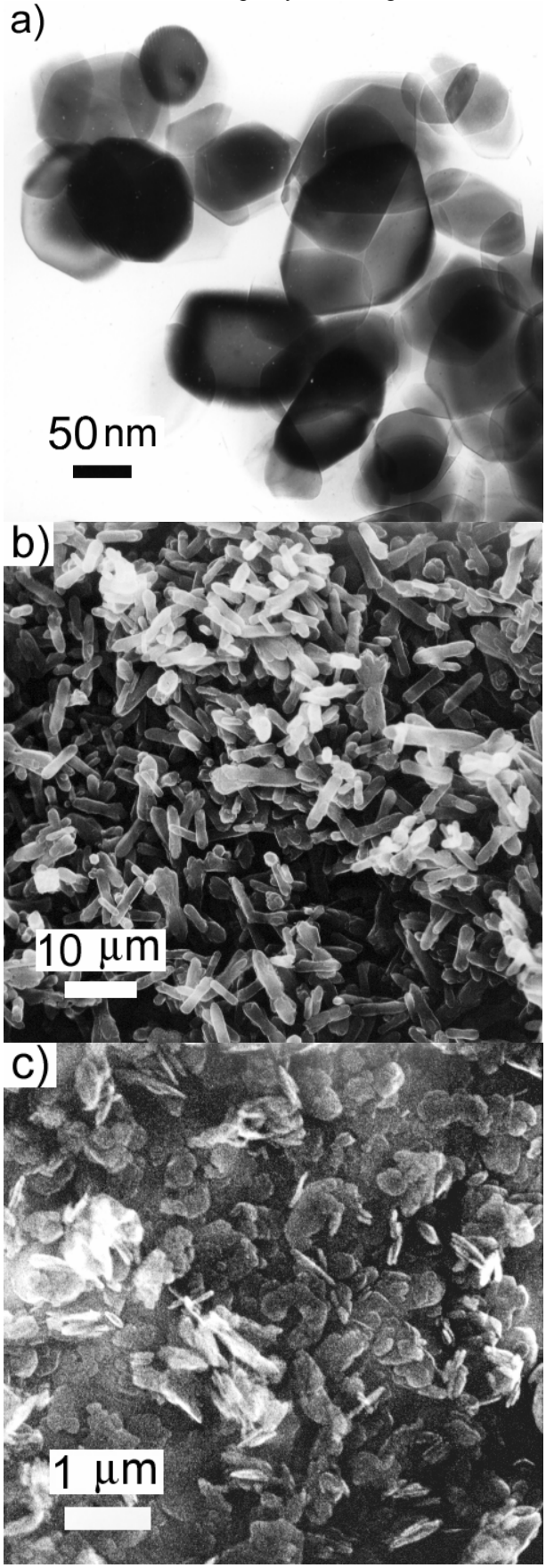

Fig.1. Transmission TEM (a, α-Fe_2O_3) and scanning electron micrographs (b, ZnO; c, NiO) of simple oxide, prepared under hydrothermal conditions.

In order to establish an appropriate pH for the hydrothermal synthesis (t=250°C, τ=6 h,) of nickel-zinc ferrite $Ni_{0,5}Zn_{0,5}Fe_2O_4$ from the amorphous gel containing the hydroxides of both metals the synthesis was performed at 3 different pH (7.0; 8.0 and 9.0) followed by the chemical analysis of aqueous solutions separated from the ferrite formed. This examination demonstrated that the pH=8 is optimal. At this pH the minimum quantities of nickel and zinc (about 2.0 %) were detected in aqueous solution. This pH value is quite close to the one used in [6] for the hydrothermal synthesis of $Mn_{0,5}Zn_{0,5}Fe_2O_4$: pH=8,6 (t=140°C, τ=2 h) and pH=8,2 (t=200°C, τ=2 h). At pH=7 and 9 the nickel and zinc losses are considerable and reach 8-10 %. This fact agrees quite well with XRD data, which show the presence of α-Fe_2O_3 together with the principal spinel phase (Fig.2.).

According to the results of our research the nickel-zinc ferrites $Ni_{0,5}Zn_{0,5}Fe_2O_4$ and $Ni_{0,2}Zn_{0,8}Fe_2O_4$ were prepared at pH=8.0. Their compositions were confirmed by means of chemical analysis.

Table 2. Hydrothermal synthesis conditions and crystallite size of prepared ferrites.

N	Sample composition	Synthesis conditions	Mean crystallite size determined by XRD/TEM
1	$ZnFe_2O_4$	t=230°C, τ=6 h, pH=8,0	13/18
2	$NiFe_2O_4$	t=130 °C, τ=1 h, pH=9,0	9/12
3	$NiFe_2O_4$	t=150 °C, τ=1 h, pH=9,0	10/14
4	$NiFe_2O_4$	t=230°C, τ=6 h, pH=9,0	14/19
5	$Ni_{0.2}Zn_{0.8}Fe_2O_4$	t=230°C, τ=6 h, pH=8,0	13/18
6	$Ni_{0,5}Zn_{0.5}Fe_2O_4$	t=230°C, τ=6 h, pH=8,0	12/16

The DTA results for the ferrites obtained show the absence of exothermal peaks which is evidence of crystallinity of the samples. According to TG data the water elimination is a two-step process: at 100-150°C the principal weight loss is obseved related to the elimimation of adsorbed and chemisorpted water, at 300-350°C the structure-bound water is eliminated. The weight loss up to 1000°C is 3-6 % of initial mass and decreases with the increase in temperature and duration of hydrothermal synthesis.

The TEM pictures of the ferrites obtained are represented in Fig. 3. The average crystallite sizes determined from SEM data and XRD peak broadening coincide well (Table 2).

As it can be seen for nickel ferrite (samples 2, 3 and 4, table 2), the decrease in temperature and duration of

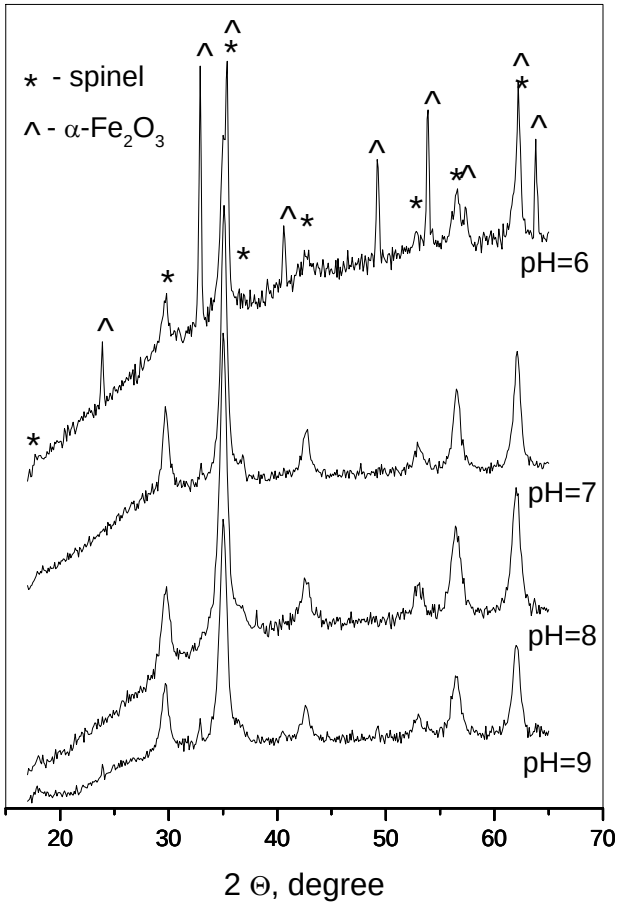

Fig.2. XRD patterns of zinc ferrites prepared at 250°C, 6 hours and various pH values.

hydrothermal synthesis leads to the formation of more dispersed $NiFe_2O_4$ powders.

The magnetic susceptibility measurements in alternating magnetic field (χ) for nanosized $NiFe_2O_4$ are represented in Fig. 4 (temperature range 20-298 K).

The maxima typical for superparamagnetic particles [7] are observed on the (χ-T) dependence. The corresponding maximum temperature called average blocking temperature (T_b) increases with the average crystallite size for the samples with the same composition. It can be clearly observed for 3 samples of nickel ferrite (samples 2, 3 and 4) with the crystallite size 12, 14, 19 nm respectively (according to TEM data). The corresponding T_b values are 200, 260K but for sample 4 (table 2) the maximum does not appear up to 300 K (fig. 4). The absence of this maximum on χ-T curve is evidence of the fact the average crystallite size (19 nm) is bigger than the critical one (D_{cr}) for nickel ferrite corresponding to the appearance of superparamagnetic properties. The D_{cr} value for $NiFe_2O_4$ might come to 15-16 nm, which agrees with the data previously obtained (10-16 нм) [8] and defines them more precisely. For nickel-zinc ferrite $Ni_{0,2}Zn_{0,8}Fe_2O_4$ (average crystallite size D=18 nm) T_b is equal to 215K and for $Ni_{0,5}Zn_{0,5}Fe_2O_4$ – 285K (D= 16 nm, table 2).

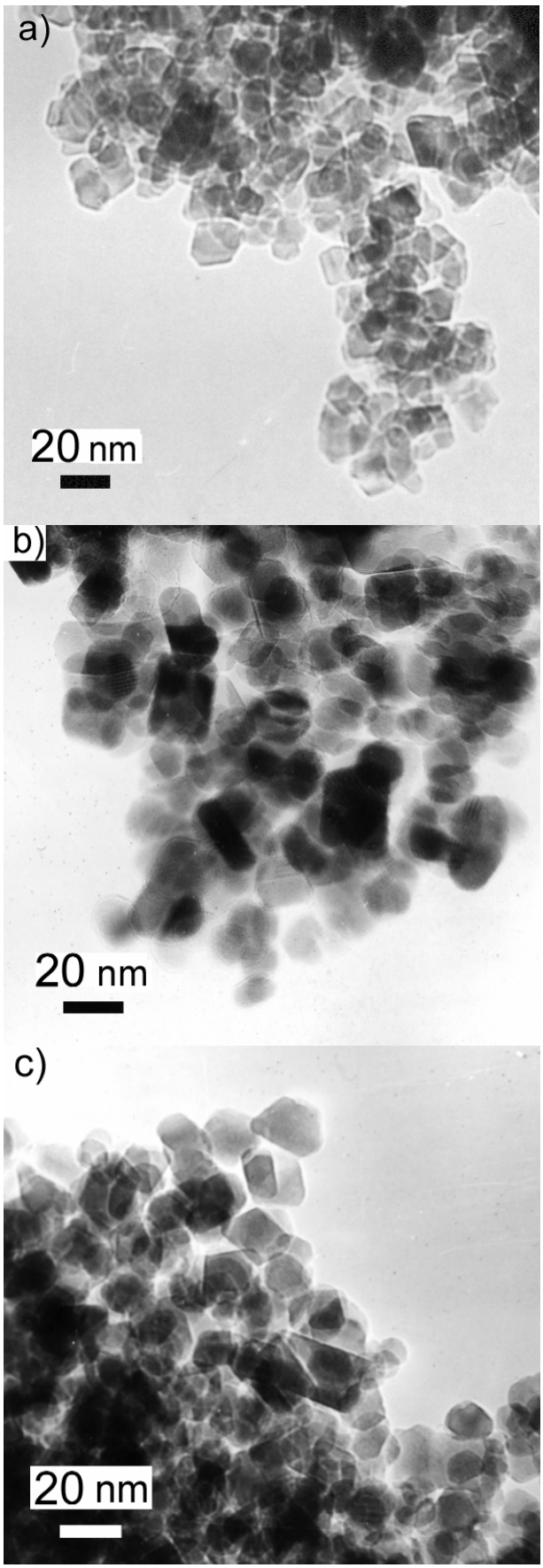

Fig.3. TEM images of prepared nanocrystalline ferrites. a)- $ZnFe_2O_4$, b)- $NiFe_2O_4$, c)- $Ni_{0.2}Zn_{0.8}Fe_2O_4$; samples 1, 4, 5 respectively (Table 2.).

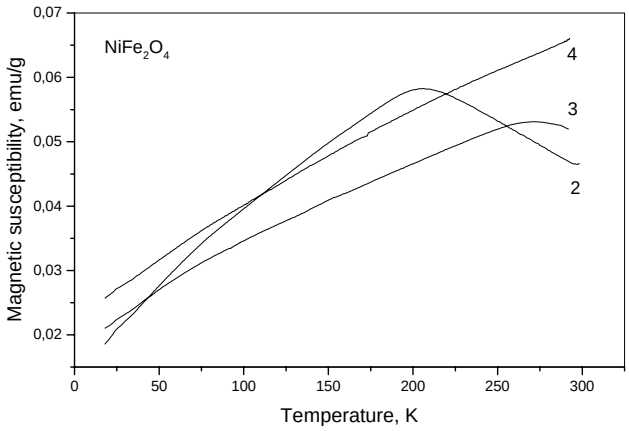

Fig.4. Temperature dependencies of specific magnetic susceptibility for nickel ferrite samples (N 2, 3, 4 Table 2) synthesized at various temperatures and time of treatment.

Hence in the present work the nanosized powdes (10-20 nm) of Zn, Ni, Ni-Zn ferrites, iron (III), nickel and zinc oxides are synthesized. The physical, chemical and magnetic properties of the samples obtained are investigated. It is demonstrated that the nanosized powders of Ni and Ni-Zn ferrites exhibit superparamagnetic properties.

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4. References

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