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Reactivity of 3d Transition Metal Cations in Diethylene Glycol Solutions. Synthesis of Transition Metal Ferrites with the Structure of Discrete Nanoparticles Complexed with Long-Chain Carboxylate Anions

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Study of the reactivity of 3d transition metal cations in diethylene glycol solutions revealed several key features that made it possible to develop a new method for synthesis of the nanocrystalline transition metal ferrites. The 3–7 nm particles of $\{MFe_2O_4\}_n[O_2CR]_m$, where M = Mn, Fe, Co, Ni, and Zn, ligated on their surface with long-chain carboxylate anions, have been obtained in an isolated yield of 75–90%. The key features are the following. Complexation of the first-row transition metal cations with diethylene glycol at a presence of alkaline hydroxide is sufficient to enable control over the rate of their hydrolysis. The reaction of hydrolysis leads to the formation of metal oxide nanocrystals in colloidal solution. The nanoparticles growth is terminated by an added long-chain carboxylic acid, which binds to their surface and acts as a capping ligand. The isolated nanocrystalline powders are stable against agglomeration and highly soluble in nonpolar organic solvents.

Introduction

Transition metal ferrites are well-established materials for application due to their useful magnetic properties. Their composition, both elemental and stoichiometric, is easily altered without major structural changes, which permits tuning their ferrimagnetic properties in a wide range. Bringing the dimensionality of ferrites to a nanometer scale opens up new windows for their application, including high-density memory devices, ferrofluids, drug carriers, MRI contrast agents, etc.[1] High stability in different chemical environment, compared to metallic nanoparticles, makes ferrites particularly useful for biological and medical applications. Most of these areas require nanomaterials with the structure of discrete nanoparticles that can be dispersed or dissolved in some common solvents. Synthesis of nanocrystalline ferrites has been achieved using microemulsion techniques, where agglomeration is suppressed by the micellar structure of the reaction fluids.[2] However once products are liberated from solvent and surfactant, the resulting nanopowders would not be soluble in regular solvents. Solubility is one of the biggest challenges since nanocrystals of metal oxides tend to agglomerate due to their large surface energy. It is possible to solve this problem by passivating the surface of the (nano)crystal by attaching capping ligands. There are a number of reports on successful synthesis of nanoparticles of metals[3] and metal chalcogenides[4] stabilized by complexing with ligands containing

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long hydrocarbon chains. However, only a few publications deal with soluble nanoparticles of metal oxides.[5]

Although the developed methods for synthesis of capped metal oxides are reported to produce high-quality nanoparticles, their industrial application is questionable for a number of reasons. Generally, the existing methods are not scalable because of the (a) hazardous nature of precursors, (b) hazardous or complicated process, (c) high cost of the materials, and/or (d) low product yield. The latter issue is worth pointing out with a special emphasis, since analysis of the literature data indicates that the yield of nanocrystalline products is rarely reported.

In this work, we intended to develop a new method for synthesis of transition metal ferrites with the structure of discrete nanoparticles. This method was supposed to provide a high product yield, be versatile enough so that different metals can be used, and be easily scalable. To ensure the nanocrystalline state of the ferrites, their surface metal atoms would be complexed with capping ligands containing hydrocarbon chains of variable lengths as substituents.

An initial issue for the designed strategy was to find a way to control kinetics of the nanoparticles growth. After evaluation of different types of reactions, we excluded ion metathesis reactions that usually run instantaneously yielding precipitates of a random morphology. The reaction of our choice is the hydrolysis of metal complexes that can be performed in nonaqueous solutions. It seems that the rate of this reaction might be adjusted by variating either the concentration of water in nonaqueous solutions or the temperature. The nonaqueous approach seems also to be beneficial for solving the problem of the nanocrystals surface composition. The typical reaction of hydrolysis, $M^{n+} + 2H_2O \leftrightarrows M(OH)^{(n-1)+} + H_3O^+$, is reversible since free acid formed in it shifts the equilibrium to the left. To provide a high yield of the products, the hydrolysis reactions were performed in the presence of a stoichiometric amount of an additional reagent that acted as a proton trap.

Experimental Section

General Methods. Syntheses were carried out using Schlenk technique under argon. The air-sensitive chemicals were manipulated in a VAC glovebox with a nitrogen atmosphere. Chemicals and solvents were used as received from Aldrich, $ZnCl_2$ 98%, $FeCl_2\cdot 4H_2O$ 99%, $CoCl_2\cdot 6H_2O$ 98%, $FeCl_3\cdot 6H_2O$ 97%, $MnCl_2\cdot 4H_2O$ 98+%, $CuCl_2\cdot 2H_2O$ 99+%, NaOH 97% (20−40 mesh beads), diethylene glycol 99%, myristic acid 99.5%, oleic acid 90%, phenyl ether 99%, and methyl alcohol 99.8%, and from Alfa Aesar, $CoCl_2$ 99.7%, $CoBr_2$ (Co 26.6%), $NiCl_2\cdot 6H_2O$ 99.3%, and $NaOCH_3$ 98%.

The IR spectra were obtained on a Perkin-Elmer 1600 spectrometer; the samples were prepared as KBr pellets. The powder X-ray diffraction (XRD) measurements were performed using a Phillips X'pert system equipped with a graphite monochromator (Cu Kα radiation). Electron microscopy (TEM), EDS, and SAD were preformed on a JEOL 2010. The samples were prepared by depositing the toluene solutions of nanoparticles on the carbon grids and drying. Elemental analysis was performed by Galbraith Laboratories, Inc.

Preparation of Metal Ferrite Nanoparticles by the Room-Temperature Method a. A 1 mmol amount of $MCl_2\cdot nH_2O$ (M = Fe, Co, or Zn) and 2 mmol of $FeCl_3\cdot 6H_2O$ were dissolved in 10 g of diethylene glycol in a Schlenk flask under protection with argon. Separately, 8 mmol of NaOH was dissolved in 10 g of diethylene glycol. A solution of NaOH was added to solution of metal chlorides while stirring at room temperature causing an immediate color change. A mixture of 3.00 g of water in 3.00 g of diethylene glycol was added to the above solution. As the liquid turned turbid, the reaction was stopped by adding 1 mmol of myristic acid dissolved in 10 mL of methanol. This addition caused immediate precipitation of solids. The mixture was stirred for 30−60 min at room temperature and then centrifuged. The precipitate was washed with methanol and redissolved in 20 mL of phenyl ether. The resulting solution was thermally treated in a Schlenk flask under protecting flow of argon. The temperature was raised to 220 °C in the course of 30 min and kept for another 10 min. After cooling, the solution was mixed with 1−2 volumes of methanol and the precipitate was separated by centrifuging, washed with methanol, and dried under opened air or stored moistened with methanol. A typical yield of dark brown powders was 0.35−0.40 g. Powder X-ray diffraction data were consistent with a spinel structure.

Preparation of Metal Ferrite Nanoparticles by the Elevated-Temperature Methods b and c. $MnFe_2O_4$ (Method b). A 2 mmol amount of $MnCl_2\cdot 4H_2O$ and 4 mmol of $FeCl_3\cdot 6H_2O$ were dissolved in 20 g of diethylene glycol in a Schlenk flask under protection with argon. Separately, 16 mmol of NaOH was dissolved in 40 g of diethylene glycol. A solution of NaOH was added to solution of metal chlorides while stirring at room temperature causing an immediate color change. After 4 h, the temperature of solution was raised during 1 h to 210−220 °C and then kept constant for 0.5 h. As the solution turned turbid, the reaction was terminated by adding 2.3 mmol of oleic acid dissolved in 20 g of DEG. This addition caused immediate precipitation of solids. The mixture was cooled to room temperature and then centrifuged. The precipitate was washed with methanol and redissolved in 20 mL of toluene. The resulting solution was centrifuged and mixed with 1−2 volumes of methanol. The precipitate was separated by centrifuging, washed with methanol, and dried under opened air or stored moistened with methanol. The yield of dark brown powder was 0.53 g.

$MnFe_2O_4$ (Method c). A 1 mmol amount of $MnCl_2\cdot 4H_2O$ and 2 mmol of $FeCl_3\cdot 6H_2O$ were dissolved in 50 g of diethylene glycol in a Schlenk flask under protection with argon. Separately, 8 mmol of NaOH was dissolved in 40 g of diethylene glycol. A solution of NaOH was added to solution of metal chlorides while stirring at room temperature causing an immediate color change. After 4 h, the temperature of the resulting solution was raised during 1 h to 200−210 °C and then kept constant for 0.5 h. As the solution turned turbid, the reaction was terminated by adding 1 mmol of oleic acid dissolved in 20 g of DEG. This addition caused immediate precipitation of solids. The mixture was cooled to room temperature and then centrifuged. The precipitate was washed with methanol and redissolved in 10 mL of toluene. The resulting solution was centrifuged and mixed with 1−2 volumes of methanol. The precipitate was separated by centrifuging, washed with methanol, and dried under opened air or stored moistened with methanol. The yield of dark brown powder was 0.25 g.

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$FeFe_2O_4$ (Method b). A 2 mmol amount of $FeCl_2 \cdot 4H_2O$ and 4 mmol of $FeCl_3 \cdot 6H_2O$ were dissolved in 40 g of diethylene glycol in a Schlenk flask under protection with argon. Separately, 16 mmol of NaOH was dissolved in 40 g of diethylene glycol. A solution of NaOH was added to solution of metal chlorides while stirring at room temperature causing an immediate color change. The temperature of the resulting solution was raised during 1−1.5 h to 210−220 °C and then kept constant for 0.5−1 h. As the solution turned turbid, the reaction was terminated by adding 2.6 mmol of oleic acid dissolved in 20 g of DEG. This addition caused immediate precipitation of solids. The mixture was cooled to room temperature and then centrifuged. The precipitate was washed with methanol and redissolved in 20 mL of toluene. The resulting solution was centrifuged and mixed with 1−2 volumes of methanol. The precipitate was separated by centrifuging, washed with methanol, and dried under opened air or stored moistened with methanol. The yield of dark brown powder was 0.511 g.

$CoFe_2O_4$ (Method b). A 2 mmol amount of $CoCl_2 \cdot 6H_2O$ and 4 mmol of $FeCl_3 \cdot 6H_2O$ were dissolved in 20 g of diethylene glycol in a Schlenk flask under protection with argon. Separately, 16 mmol of NaOH was dissolved in 20 g of diethylene glycol. A solution of NaOH was added to solution of metal chlorides while stirring at room temperature causing an immediate color change. After 1 h, the temperature of solution was raised during 1.5 h to 180−190 °C and then kept constant for 1 h. As the solution turned turbid, the reaction was terminated by adding 2 mmol of oleic acid dissolved in 20 g of DEG. This addition caused immediate precipitation of solids. The mixture was cooled to room temperature and then centrifuged. The precipitate was washed with methanol and redissolved in 20 mL of toluene. The resulting solution was centrifuged and mixed with 1−2 volumes of methanol. The precipitate was separated by centrifuging, washed with methanol, and dried under opened air or stored moistened with methanol. The isolated yield of dark brown powder was 0.5 g.

$CoFe_2O_4$ (Method c). A 2 mmol amount of $CoCl_2 \cdot 6H_2O$ and 4 mmol of $FeCl_3 \cdot 6H_2O$ were dissolved in 40 g of diethylene glycol in a Schlenk flask under protection with argon. Separately, 16 mmol of NaOH was dissolved in 40 g of diethylene glycol. A solution of NaOH was added to solution of metal chlorides while stirring at room temperature causing an immediate color change. After 2−2.5 h, the temperature of the resulting solution was raised during 1 h to 220 °C and then kept constant for 0.5 h. As the solution turned turbid, the reaction was terminated by adding 2.5 mmol of oleic acid dissolved in 20 g of DEG. This addition caused immediate precipitation of solids. The mixture was cooled to room temperature and then centrifuged. The precipitate was washed with methanol and redissolved in 20 mL of toluene. The resulting solution was centrifuged and mixed with 1−2 volumes of methanol. The precipitate was separated by centrifuging, washed with methanol, and dried under opened air or stored moistened with methanol. The isolated yield of dark brown powder was 0.5 g.

$NiFe_2O_4$ (Method b). A 2 mmol amount of $NiCl_2 \cdot 6H_2O$ and 4 mmol of $FeCl_3 \cdot 6H_2O$ were dissolved in 20 g of diethylene glycol in a Schlenk flask under protection with argon. Separately, 16 mmol of NaOH was dissolved in 40 g of diethylene glycol. A solution of NaOH was added to solution of metal chlorides while stirring at room temperature causing an immediate color change. After 4 h, a solution 1.2 g of water + 15 g of DEG was added in three equal portions while the temperature was raised during 1−1.5 h to 200−210 °C. Finally, the temperature was kept constant for 0.5−1 h. As the solution turned turbid, the reaction was terminated by adding 2.6 mmol of oleic acid dissolved in 20 g of DEG. This addition caused immediate precipitation of solids. The mixture was cooled to room temperature and then centrifuged. The precipitate was washed with methanol and redissolved in 20 mL of toluene. The resulting solution was centrifuged and mixed with 1−2 volumes of methanol. The precipitate was separated by centrifuging, washed with methanol, and dried under opened air or stored moistened with methanol. The isolated yield of dark brown powder was 0.5 g.

$NiFe_2O_4$ (Method c). A 2 mmol amount of $NiCl_2 \cdot 6H_2O$ and 4 mmol of $FeCl_3 \cdot 6H_2O$ were dissolved in 50 g of diethylene glycol in a Schlenk flask under protection with argon. Separately, 16 mmol of NaOH was dissolved in 50 g of diethylene glycol. A solution of NaOH was added to solution of metal chlorides while stirring at room temperature causing an immediate color change. After 4 h, 1.0 g of water mixed with 10 g of DEG was added in two equal portions while temperature was raised during 1−1.5 h to 200−210 °C. Finally, the temperature was kept constant for 0.5−1 h. As the solution turned turbid, the reaction was terminated by adding 2 mmol of oleic acid dissolved in 20 g of DEG. This addition caused immediate precipitation of solids. The mixture was cooled to room temperature and then centrifuged. The precipitate was washed with methanol and redissolved in 20 mL of toluene. The resulting solution was centrifuged and mixed with 1−2 volumes of methanol. The precipitate was separated by centrifuging, washed with methanol, and dried under opened air or stored moistened with methanol. The yield of dark brown powder was 0.525 g.

$ZnFe_2O_4$ (Method b). A 1 mmol amount of $ZnCl_2$ and 2 mmol of $FeCl_3 \cdot 6H_2O$ were dissolved in 10 g of diethylene glycol in a Schlenk flask under protection with argon. Separately, 8 mmol of NaOH was dissolved in 10 g of diethylene glycol. A solution of NaOH was added to solution of metal chlorides while stirring at room temperature causing an immediate color change. After 2−2.5 h, the temperature of the resulting solution was raised during 1 h to 210 °C and then kept constant for another1 h. As the solution turned turbid, the reaction was terminated by adding 1.25 mmol of oleic acid dissolved in 10 g of DEG. This addition caused immediate precipitation of solids. The mixture was cooled to room temperature and then centrifuged. The precipitate was washed with methanol and redissolved in 20 mL of toluene. The resulting solution was centrifuged and mixed with 1−2 volumes of methanol. The precipitate was separated by centrifuging, washed with methanol, and dried under opened air or stored moistened with methanol. The isolated yield of a brown powder was 0.32 g.

$ZnFe_2O_4$ (Method c). A 2 mmol amount of $ZnCl_2$ and 4 mmol of $FeCl_3 \cdot 6H_2O$ were dissolved in 40 g of diethylene glycol in a Schlenk flask under protection with argon. Separately, 16 mmol of NaOH was dissolved in 40 g of diethylene glycol. A solution of NaOH was added to solution of metal chlorides while stirring at room temperature causing an immediate color change. After 2−2.5 h, the temperature of the resulting solution was raised during 1 h to 210 °C and then kept constant for another1 h. As the solution turned turbid, the reaction was terminated by adding 2.5 mmol of oleic acid dissolved in 20 g of DEG. This addition caused immediate precipitation of solids. The mixture was cooled to room temperature and then centrifuged. The precipitate was washed with methanol and redissolved in 20 mL of toluene. The resulting solution was centrifuged and mixed with 1−2 volumes of methanol. The precipitate was separated by centrifuging, washed with methanol, and dried under opened air or stored moistened with methanol. The isolated yield of a brown powder was 0.5 g.

Results and Discussion

The newly designed method is different from currently available methods by its controlled stepwise character. Every step is responsible for a particular process, such as (a) metal complexation, (b) hydrolysis/condensation, and (c) terminating/capping ligation.

We found that diethylene glycol (DEG) can function as a complexing agent and a solvent for performing the synthesis. It remains liquid in a wide range of temperatures (−10 to 245 °C) and has a high dielectric constant ($\epsilon = 32$) that enables it to dissolve polar and ionic substances. In addition, the structure of its molecule is ideal for forming chelated complexes with metals, either neutral or anionic when its molecules are deprotonated. Application of DEG as a solvent was reported for synthesis of ZnO nanopowder by thermal decomposition of zinc acetate hydrate.[6]

Many of the first-row transition metal chlorides, both hydrated and anhydrous, are soluble in DEG, and this property was used for preparing their 0.1 or 0.2 *m* stock solutions. The tested cations include Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}. Anhydrous sodium hydroxide is also soluble in DEG, and its stock 0.8 *m* solution was used to perform reactions with metal precursors. Mixing both solutions in equivalent quantities usually causes immediate color change (in case of open-shell cations) without precipitation of any solids in all cases except for Cu^{2+}. In the case of DEG and $CoCl_2{\cdot}6H_2O$, we found that its original 0.1 *m* deep blue solution turns to deep purple upon addition of 2 equiv of NaOH. The resulting solution is air-sensitive and turns brown on contact with oxygen. This can be explained by an increased energy splitting between metal orbitals (like between t_{2g} and e_g in octahedral complexes) when the softer ligands are replaced with the harder ones. Evidently, this facilitates oxidation of d^7 Co^{2+} into d^6 Co^{3+} cation.

The reaction between $CoCl_2$ and NaOH was also tested in solutions of different polyols such as ethylene glycol and 1,1,1-tris(hydroxymethyl)propane (50% solution in ethanol), and it was found that precipitation of cobalt hydroxo salts (or hydroxide) occurs instantaneously. This indicates the unique chelating properties of DEG that help to stabilize the complexed Co^{2+} in basic solution.

We propose two alternative scenarios for this observation. According to one, the softer Cl^- ligands are substituted with the harder OH^- in the inner sphere, but the metal atom remains chelated with DEG; according to the other, Cl^- ligands remain intact, but chelated complex becomes deprotonated, so that the softer alcohol ligand is converted into the harder alkoxide. To identify the right path, similar reaction (with Co^{2+}) was performed in a different solvent, diethylene glycol monobutyl ether, that cannot form a dianion as DEG does but has the same chelating strength. Mixing solutions of cobalt chloride and sodium hydroxide in this solvent caused immediate precipitation of cobalt hydroxy salts or cobalt hydroxide. This observation indicates that hydroxo groups of DEG are involved in the process and, thus, supports the second mechanism (Scheme 1a). We also observed that precipitation of metal oxides does not happen even when the alkaline DEG solutions of anhydrous salts are heated to temperatures above 200 °C. This probably would be different with a neutral dihydroxo complex and an alcohol form of DEG. Another method for identification of the reaction pathway would be spectroscopic, but unfortunately, due to band broadening, evaluation of the UV−vis spectra of DEG solutions containing $CoBr_2$ instead of $CoCl_2$ and $NaH(OCH_2CH_2)_2O$ or $NaOCH_3$ instead of NaOH was inconclusive.

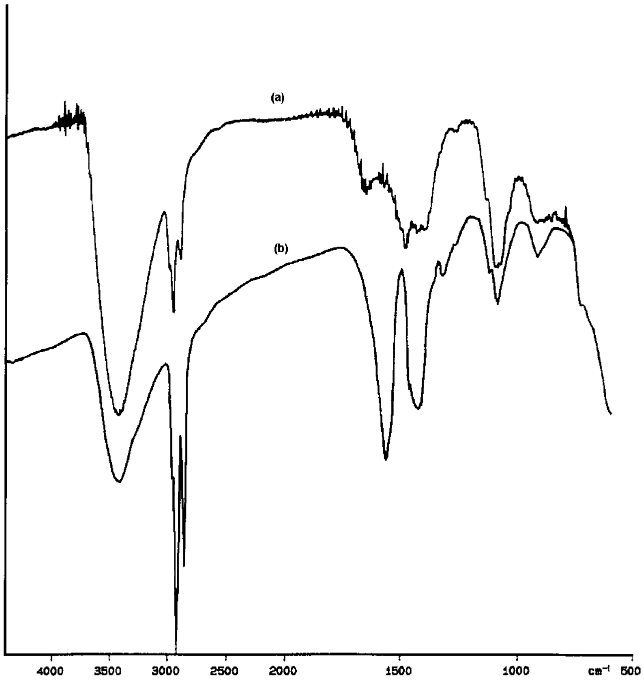
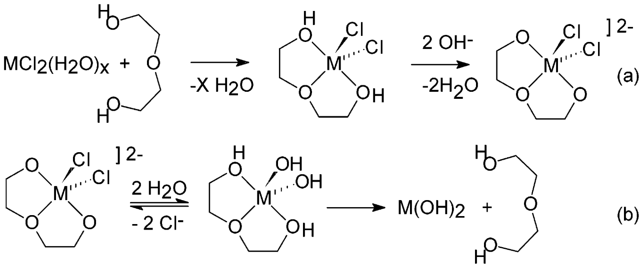


Figure 1. IR spectra of (a) intermediate product $ZnFe_2O_4$ containing DEG and (b) zinc ferrite capped with myristate anion and obtained by the room-temperature method.

Scheme 1. Proposed Scheme for Complex Formation (a) and Its Hydrolysis (b) in DEG Solution



Scheme 2. Dehydration of the Nanoparticles Cores

$$\{M(OH)_2{+}2Fe(OH)_3\}_X[O_2CR]_Y \rightarrow \{MFe_2O_4\}_X[O_2CR]_Y + 8x\ H_2O$$

The metal DEG complexes undergo nucleophilic substitution reactions when the temperature or concentration of water in the system is increased. This causes the beginning of condensation of mononuclear hydroxide reactive intermediates and eventually leads to precipitation of metal hydroxides or oxides (Scheme 1b). The advantage of this method over a simple ion metathesis reaction is that the rate of nucleophilic substitution reaction with neutral molecules of water is much lower. The crystal growth is slow enough to be monitored visually or using optical methods, and this process can be stopped at any moment. The reaction is terminated

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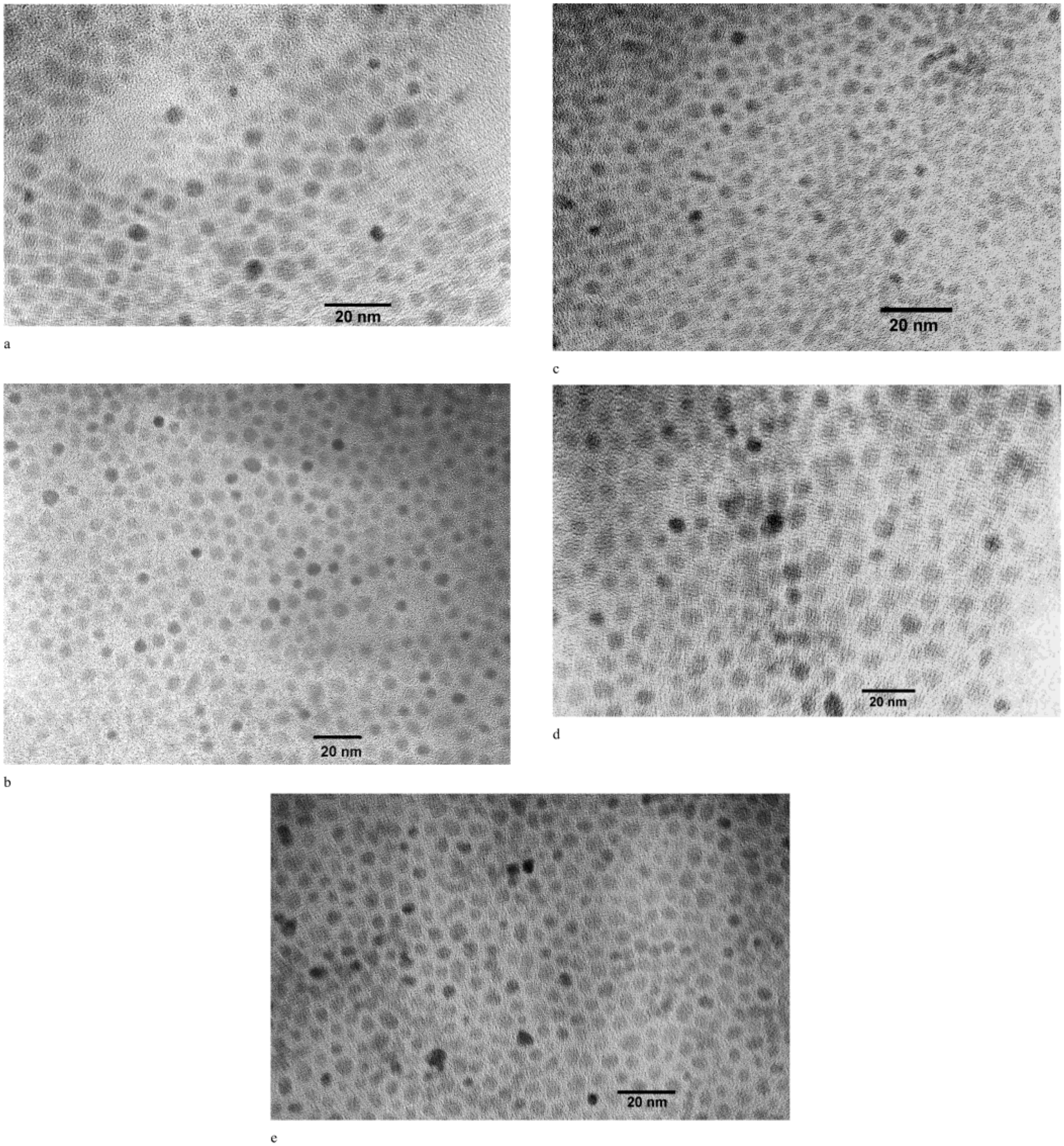

Figure 2. TEM images of ferrite nanoparticles: (a) $MnFe_2O_4$ (method c); (b) $FeFe_2O_4$ (b); (c) $CoFe_2O_4$ (c); (d) $NiFe_2O_4$ (c); (e) $ZnFe_2O_4$ (c).

by adding a capping ligand that binds to the surface of growing nanoparticles and passivates it. Due to long hydrocarbon chains of capping ligands, the nanoparticles become insoluble in highly polar solvent DEG and immediately precipitate. We tested several long-chain carboxylates for their activity and found that in a form of sodium salts they did not react with metal oxide nanoparticles; only corresponding acids were reactive. In this study oleic $CH_3(CH_2)_7$-$CHCH(CH_2)_7COOH$ and myristic $CH_3(CH_2)_{12}COOH$ acids were used as capping ligands.

The described results have been used as a base for synthesis of the nanoscale metal oxides $M^{II}Fe^{III}{}_2O_4$ that have a cubic structure of spinel or inversed spinel as bulk solids. Solutions of two metal salts, $FeCl_3$ and MCl_2 (M = Mn, Fe, Co, Ni, and Zn), were used in stoichiometric ratio 2:1. We also tried to synthesize nanoparticles of γ-Fe_2O_3 that has the same crystal structure.

Synthesis of Ferrite Nanoparticles by Room-Temperature Hydrolysis. This method was applied for synthesis of Fe, Co, and Zn ferrites. The DEG solution of metal

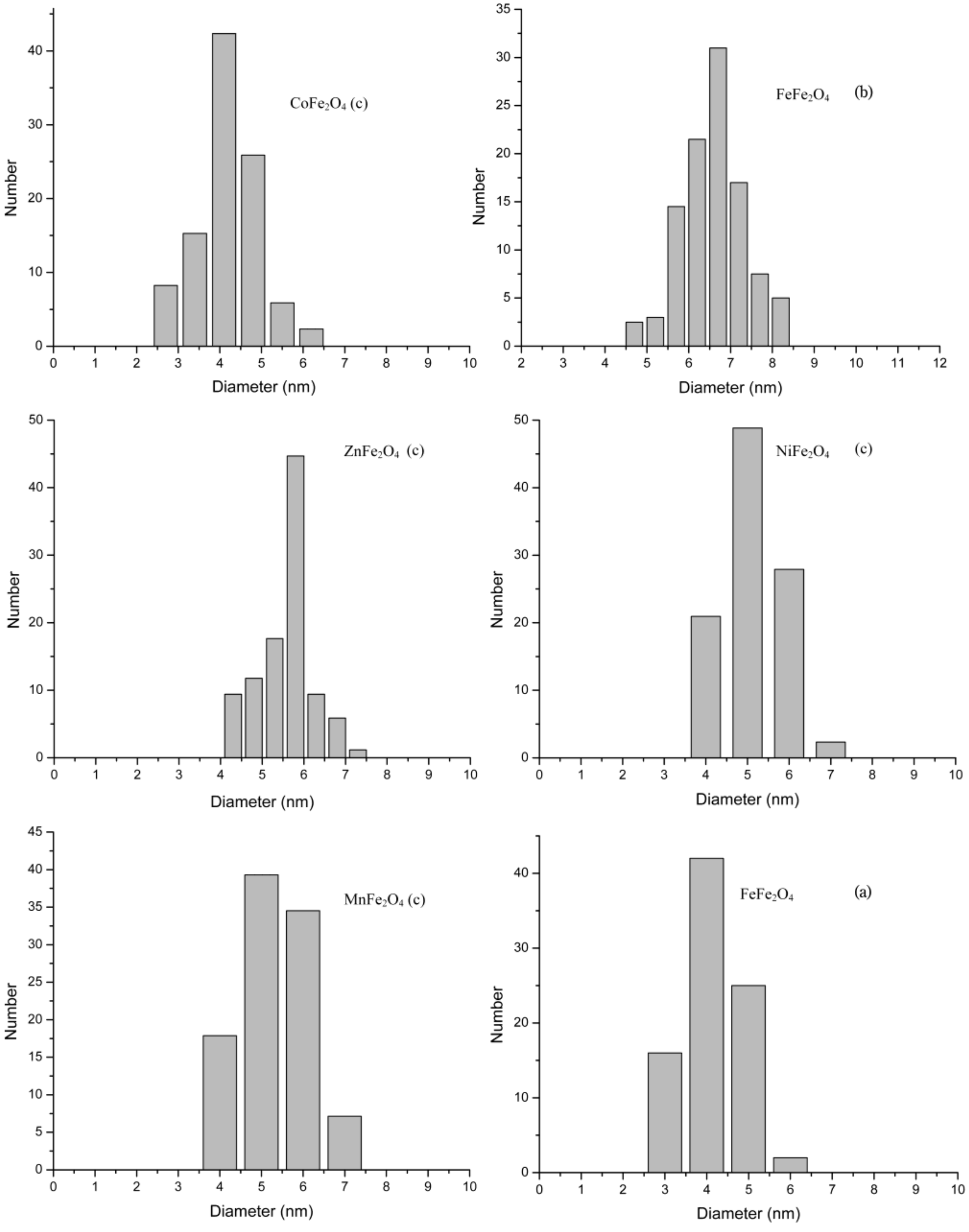

Figure 3. Ferrite nanoparticles size distribution.

chlorides containing a stoichiometric quantity of sodium hydroxide is treated with water (2−3 g/20 mL of reaction solution) mixed with equal amount of DEG. The reaction of hydrolysis was performed at room temperature, and as the solution turned turbid, the capping agent (myristic acid) dissolved in methanol was added to stop the reaction. The precipitated nanoparticles contained cores with mixed-metal hydroxides that were still partially ligated with DEG (this was evidenced by IR spectra) and had low crystallinity. To convert them into crystalline oxide nanoparticles, thermal treatment was necessary. For obtaining bulk metal oxides, corresponding powdered hydroxides usually undergo thermal treatment; dehydration is accompanied by crystallization. In our work we intended to preserve the identity of our products as nanocrystalline, and we also needed to obtain them as individual nanoparticles soluble in organic solvents. This is why a conventional thermal dehydration of the powders could not be used. Since our raw products were colloidal hydroxides stabilized with long-chain carboxylates, they were soluble in different nonpolar solvents. We attempted to perform their dehydration and crystallization by thermal treatment in solutions of high-boiling low-polar solvents (Scheme 2). We tested 1-decanol, butoxyethoxyethanol (bp 231 °C), and phenyl ether (bp 259 °C) and found the latter to be most convenient. A temperature of 220−250 °C appeared to be sufficient. The resulting nanocrystalline products were stable against aggregation and remained in solution. To isolate them, 1−2 volumes of methanol were added to the solution at room temperature. The suspensions were centrifuged, and the solids were washed with methanol.

Synthesis of Ferrite Nanoparticles by the Elevated-Temperature Hydrolysis. This method was applied for synthesis of Mn, Fe, Co, Ni, and Zn ferrites. The high boiling point of diethylene glycol (245 °C) allowed performing the reactions of hydrolysis at elevated temperature. This modification of the process requires a smaller quantity of water present in solution; in the case of Mn^{2+}, Fe^{2+}, Co^{2+}, and Zn^{2+}, no water was added in addition to those few equivalents introduced together with metal salt hydrates. The reaction solutions containing stoichiometric quantities of metal salt hydrates and sodium hydroxide were heated to 190−220 °C. As the solution turned turbid, the reaction was stopped by adding a DEG solution of capping ligand (oleic acid). This addition caused immediate decomposition of the colloid and precipitation of the product. After cooling, the product was isolated by centrifugation, washed with methanol, dissolved in toluene, and reprecipitated by adding methanol. Under such conditions, the nanoparticles formed in an anhydrous, highly crystalline form, so that additional step of annealing in solution was not necessary.

Typically, an isolated yield of the nanopowders after air-drying was 75−90% (calculated after metal oxide content was determined). Dry powders were highly soluble in toluene producing deep brown solutions that exhibited neither turbidity nor a Tyndall effect with a laser beam and were stable for indefinitely long time. These systems can be considered as colloidal in terms of size of the dispersed phase. On the other hand, they are stabilized similarly to molecular systems rather than colloidal with electric double layers. For this reason we use in this paper the term "solution" but not a "dispersion".

Identification of the ligand composition of the nanoparticles was done using IR spectrometry. Figure 1a shows the spectrum (in KBr pellet) of the intermediate product $ZnFe_2O_4$ containing DEG; Figure 1b shows the spectrum of zinc ferrite capped with myristate anion and obtained by the room-temperature method. This spectrum identifies long-chain carboxylate groups as well as hydroxo groups of the residual DEG or metal hydroxides. The "fingerprints" region of both spectra closely resembles the spectra of free DEG and sodium myristate, respectively.

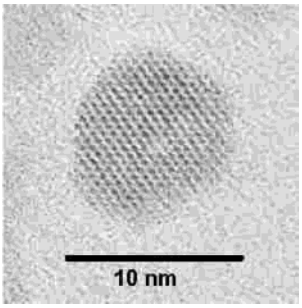

Figure 4. High-resolution TEM image of one nanoparticle of $MnFe_2O_4$.

TEM images for all obtained ferrites (labeled "c") are displayed in Figure 2a−e. As follows from these images, the particles have spherical shape and size between 3 and 7 nm for different metal ferrites and are clearly deposited apart from each other. Corresponding histograms are displayed in Figure 3. The data on mean particle size and calculated standard deviations for all metal ferrites (a−c) are given in Table 1. Products obtained by room-temperature method are labeled as (a); the elevated temperature products are labeled as (b) and (c). The main difference between products (b) and (c) is in concentration of the reaction solutions. The overall concentration of metal cations in case of (b) was 0.10−0.15 m while in case of (c) it was 0.033−0.075 *m*. The presented data indicate that there is no clear relationship between the concentration of solutions and the size and size distribution of the obtained nanoparticles.

High-resolution images often exhibit crystal lattice, as it is evident for a nanoparticle of manganese ferrite shown in Figure 4. This micrograph reveals lattice fringes for the family of planes [110] corresponding to an interlayer spacing of 0.5962 nm. This value leads to an estimated lattice parameter $a = 8.4326$ Å, which is in a good agreement with that calculated from powder X-ray data ($a = 8.439(1)$ Å) and previously reported for bulk $MnFe_2O_4$ ($a = 8.499$ Å; ASTM file No. 10-319). The image also shows a good crystallinity of the sample with absence of structural defects, such as dislocations or stacking faults.

Phase composition was evaluated using X-ray powder diffractometry; in all cases the observed pattern corresponded to crystal lattice with cubic symmetry. Diffractograms of all ferrites synthesized by the elevated temperature method are displayed in Figure 5a−e. Calculation of a particle size for $ZnFe_2O_4$ using the peak broadening gave the result of 4.6 nm, while the TEM experiment gave the value of 3 nm. The observed deviation is consistent with previously obtained results.[7]

To determine the content of metal oxides in the obtained nanopowders, we performed their quantitative analysis using a combustion method. Sintering under open air at 400−600 °C caused their complete deligation and aggregation with

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(7) Ammar, S.; Helfen, A.; Jouini, N.; Fiévet, F.; Rosenman, I.; Villain, F.; Molinié, P.; Danot, M. *J. Mater. Chem.* **2001,** *11*, 186−192.

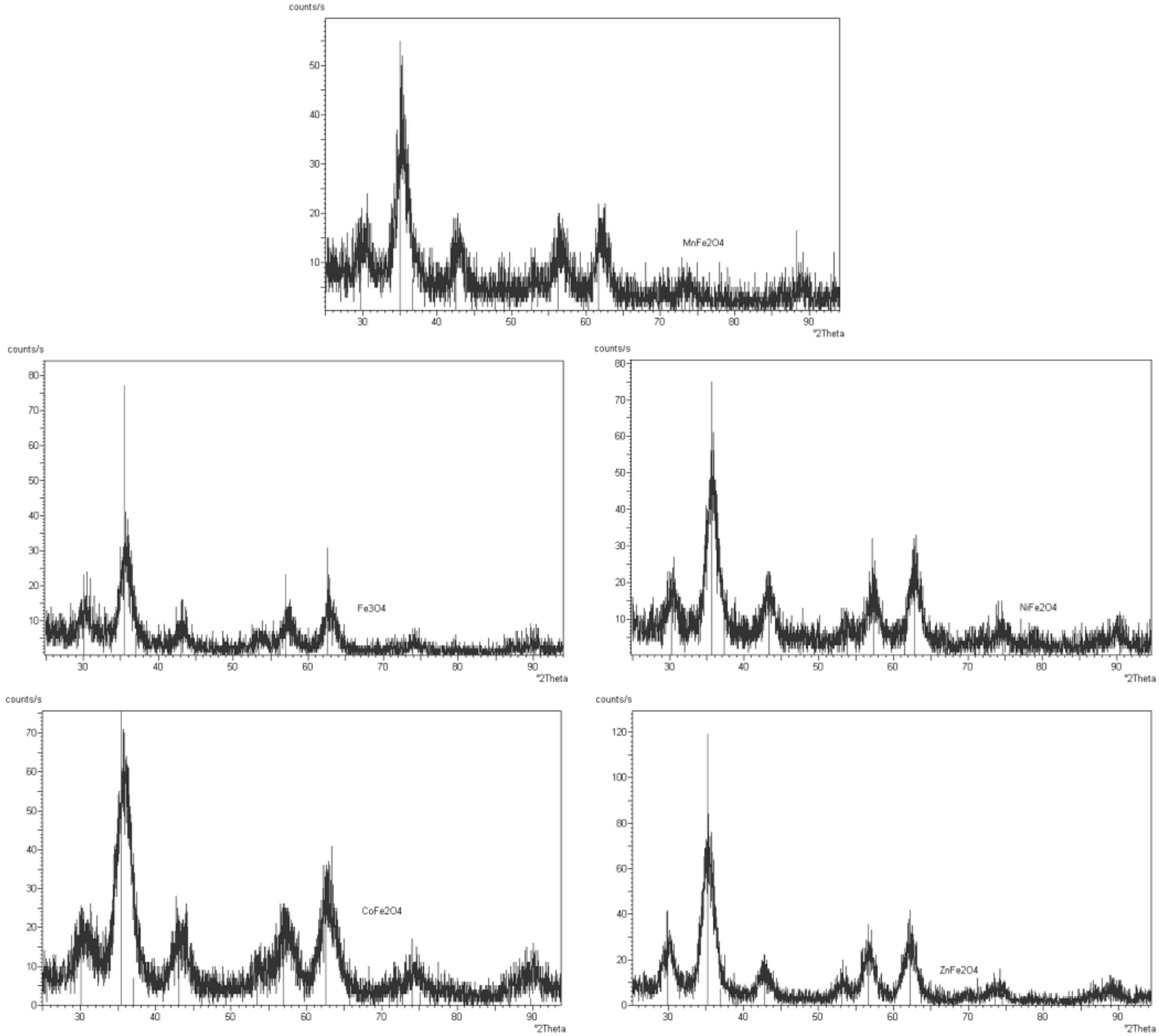

Figure 5. Typical powder X-ray diffractograms for the obtained ferrite nanopowders

formation of larger crystallites; diffractograms of both nanopowder and sintered $ZnFe_2O_4$ are displayed in Figure 6 a,b. The residual after sintering powders have been analyzed (Galbraith Laboratories, Inc.) to determine their metal ratio; the results are presented in the Table 2. Analytical and TEM data indicate that both room temperature and elevated temperature synthetic methods gave good results for iron ferrite, while, in the case of cobalt and zinc ferrites, the latter method gave products of a better quality.

Our attempt to synthesize nanoparticles of γ-Fe_2O_3 using a high-temperature method yielded the nanopowder with poor crystallinity and solubility, so that we could not get any information about its particles size.

On the basis of the obtained metal oxide content data for the sample of $CoFe_2O_4$, a molar ratio of $CoFe_2O_4$ to oleate anion was found to be 1.905:1. This corresponds to a fraction of metal atoms bearing an oleate anion of 0.175. Evidently, these atoms are located on the surface of nanocrystals. The following steps were used to calculate the percent coverage of the surface metal atoms with oleate ligands.[8] A particle diameter of 3 nm determined by TEM was used to calculate its volume. This value and a bulk density of 5.2 g/cm^3 were used to calculate the nanoparticle mass, the number of moles, the number of $CoFe_2O_4$ formula units, and finally the number of metal atoms/particle. Similar calculations were performed for a hypothetical particle derived from the original particle with a radius of 1.5 nm minus the surface atomic layer estimated as an average M−O distance of 1.95 Å. The number of metal atoms on the surface of nanoparticles was calculated by subtracting the second value from first. Finally, the fraction of these atoms over total number of metal atoms was found to be 0.34. A similar result (0.365) was obtained by using the formula $F = 4/n^{1/3}$, where F is the fraction of

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(8) Bowen Katari, J. E.; Colvin, V. L.; Alivisatos, A. P. *J. Phys. Chem.* **1994**, *98*, 4109−4117.

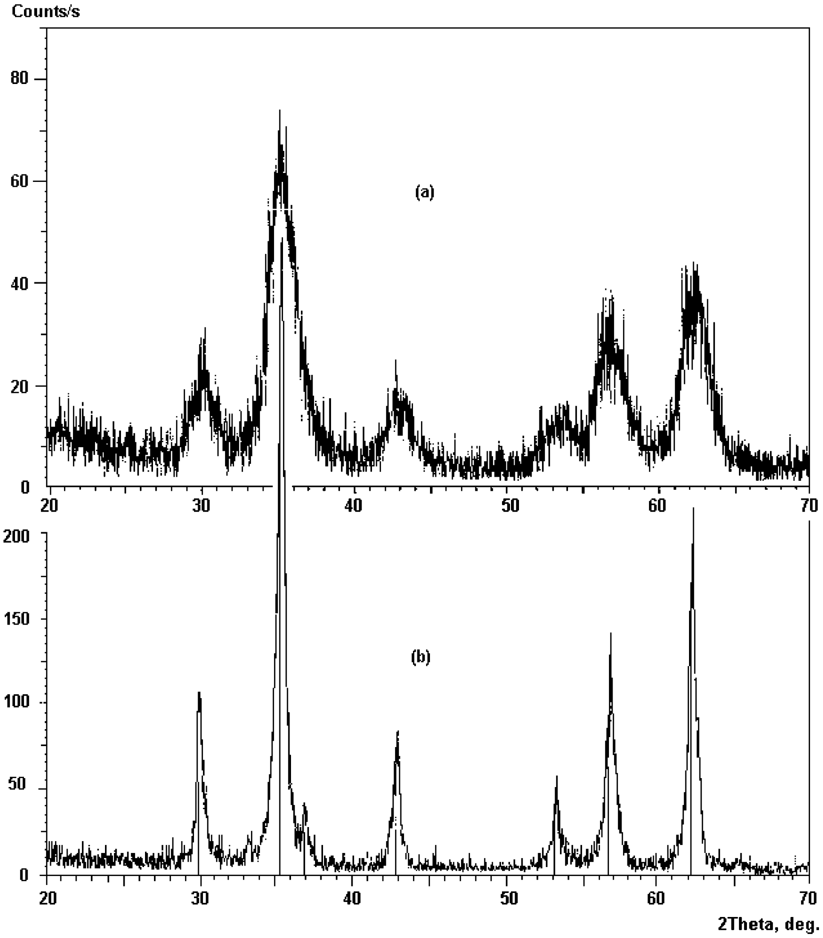

Figure 6. Powder X-ray diffractograms for $ZnFe_2O_4$: (a) 3 nm nanopowder obtained by the high-temperature method; (b) bulk solid obtained by sintering of the nanopowder.

Table 1. Size of the Particles for Synthesized Ferrites (Obtained from TEM images)

metal ferrite (method[a])	mean particle size (nm)	std dev (%)
$MnFe_2O_4$ (b)	6.6	28
$MnFe_2O_4$ (c)	5.3	16
$FeFe_2O_4$ (a)	4.2	18
$FeFe_2O_4$ (b)	6.6	11
$CoFe_2O_4$ (a)	4	*b*
$CoFe_2O_4$ (b)	3.3	10.5
$CoFe_2O_4$ (c)	4.2	18
$NiFe_2O_4$ (b)	3.6	19
$NiFe_2O_4$ (c)	5.1	15
$ZnFe_2O_4$ (a)	3	*b*
$ZnFe_2O_4$ (b)	5.1	11
$ZnFe_2O_4$ (c)	5.6	12

[a] a: obtained by room-temperature method. b and c: obtained by elevated-temperature method. [b] Accurate measurements were not possible due to the lack of sharpness.

Table 2. Results of Analysis of the Obtained Nanocrystalline Ferrites

metal ferrite (method[a])	metal oxides content (wt %)	metals content in sintered samples (wt %)	ratio of metals, Fe:M (M = Mn, Co, Ni, Zn)
$MnFe_2O_4$ (b)	78.4	Fe, 54.16; Mn, 21.03	2.53
$FeFe_2O_4$ (a)	73.9		N/A
$FeFe_2O_4$ (b)	76.4		N/A
$CoFe_2O_4$ (a)	48.7	Fe, 51.43; Co, 19.41	2.80
$CoFe_2O_4$ (b)	61.4	Fe, 50.69; Co, 24.30	2.20
$NiFe_2O_4$ (b)	69.6	Fe, 49.19; Ni, 26.09	1.98
$ZnFe_2O_4$ (a)	47.2	Fe, 48.95; Zn, 22.68	2.53
$ZnFe_2O_4$ (b)	65.2	Fe, 52.43; Zn, 24.81	2.47

[a] a: obtained by room-temperature hydrolysis method. b: obtained by elevated-temperature method.

the surface atoms and n is the total number of atoms.[9] As it was shown above, the fraction of metal atoms bearing oleate anion was 0.175, which is ~50% of all surface metal atoms. It is possible that every carboxylate anion acts as a bidentate bridging ligand that coordinates to two adjacent metal atoms.

Magnetic characterization experiments using a SQUID magnetometer for the obtained nanopowders are ongoing. All samples are superparamagnetic with the blocking temperature below 100 K (in the field 10 Oe). The observed magnetic behavior is likely to be strongly affected by a disorder of the nanoparticles surface spins. Detailed results will be published elsewhere (Tung, Spinu, Golub, et al.).

Conclusion

In this study, we developed a method for synthesis of nanocrystalline transition metal ferrites with structure of discrete nanoparticles stabilized with carboxylate capping ligands. We obtained 3−7 nm in diameter nanoparticles of Mn, Fe, Co, Ni, and Zn ferrites with isolated yield 75−90% that are soluble in low-polar organic solvents. The obtained

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(9) Edelstein, A. S.; Cammarata, R. C. *Nanomaterials: Synthesis, Properties and Applications*; Institute of Physics Publishing: Bristol, U.K., Philadelphia, PA, 1998; p 26.

products were characterized with TEM imaging, elemental analysis, and X-ray diffractometry. We believe this method can be used for the synthesis of other types of nanocrystalline metal oxides.

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