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The metamorphosis of heterometallic trinuclear antiferromagnetic complexes into nano-sized superparamagnetic spinels

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Abstract

Thermal decomposition of the trinuclear heterometallic oxoacetates $[\text{Fe}_2\text{M}(\mu_3\text{-O})(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]$ has been used as a single-precursor method for synthesis of the spinel-structured ternary oxides MFe_2O_4 ($\text{M} = \text{Mn}^{\text{II}}, \text{Co}^{\text{II}}, \text{and Ni}^{\text{II}}$). This facile process occurring at 320 °C results in the formation of nanocrystalline, (7–20 nm) highly pure stoichiometric ferrites in quantitative yield. The magnetic properties of these nanoparticulate ferrites were studied in the 10–300 K temperature range, revealing superparamagnetic behaviour for the Ni and Mn particles and ferromagnetic behavior for the Co ones at room temperature. Their blocking temperatures follow the order: $\text{CoFe}_2\text{O}_4 > \text{MnFe}_2\text{O}_4 > \text{NiFe}_2\text{O}_4$.

Keywords

A. magnetic materials; B. chemical synthesis; D. magnetometry; D. magnetic properties

1. Introduction

A variety of functional optoelectronic and magnetic materials are composed of ternary metal oxides. The common types are represented by perovskites $\text{M}^{\text{I}}\text{M}^{\text{V}}\text{O}_3$ or $\text{M}^{\text{II}}\text{M}^{\text{IV}}\text{O}_3$ and spinel ferrites $\text{M}^{\text{II}}\text{Fe}_2\text{O}_4$ with cubic crystal structure, and hexagonal ferrites $\text{M}^{\text{II}}\text{Fe}_{12}\text{O}_{19}$, etc. The performance of these materials depends on their chemical purity, structural (phase) homogeneity and morphological uniformity [1–19]. These issues are addressed as individual tasks during chemical synthesis of any desired material. Nanoscale oxide species often possess unique properties which are not typical for either the molecular or macroscopic

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scales. Their application in modern technologies potentiates connections to a number of areas of electronics, high density information storage/recording technologies, catalysis, nanomagnetic immunodiagnostics, and magnetic drug delivery [1–19].

Many existing methods for the synthesis of ternary metal oxide nanoparticles consist of several steps, commencing with co-precipitation and sintering and finally, milling. Formation of the desired crystalline phase usually occurs in heterogeneous solid state reactions, which are kinetically restricted due to slow diffusion. The more intimate the mixtures of precursors that are used, the lower the temperature and the shorter the reaction time that are needed for obtaining high-quality products. The ideal homogeneity and purity would be obtained if both constituents came from one source, and this possibility is offered by the single-molecule-precursor methods. While providing a very convenient route to high-quality products, these methods suffer from lacking of the selection of heterometallic precursor compounds. In this paper we demonstrate a new method of synthesis of spinel-type transition metal ferrites by thermal decomposition of trinuclear heterometallic oxoacetates $[\text{Fe}_2\text{M}(\mu_3\text{-O})(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Mn}^{\text{II}}$, Co^{II} , and Ni^{II}). Since a variety of these complexes containing different transition metals is available, the reported method allows preparation of nanoparticulate ferrites with $\text{M}^{\text{II}}\text{Fe}_2\text{O}_4$ ($\text{M} = \text{Mn}$, Co , Ni) compositions. Formation of pure stoichiometric ternary oxides is predetermined *a priori* by the exact $\text{M}^{\text{II}}:\text{Fe}^{\text{III}}=1:2$ ratio in the skeleton of the polynuclear precursor (Figure 1).

Another advantage of this method is that due to the low-temperature and short processing time, crystal coarsening is minimized and the products are obtained with relatively uniform nanocrystalline morphology.

2. Results

Heterometallic trinuclear oxoacetates $[\text{Fe}_2\text{M}(\mu_3\text{-O})(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Mn}^{\text{II}}$, Co^{II} , and Ni^{II}) were used as starting complexes for synthesis of the spinel-structured ferrites. The choice of precursors was based on the existence of species with the appropriate stoichiometric $\text{Fe}^{\text{III}}:\text{M}^{\text{II}}$ (2:1) molar ratio at the molecular level [20], corresponding exactly to their content in the resulting ferrites. The structural framework of heterometallic trinuclear oxocarboxylates is based on an isosceles triangular Fe_2M fragment, with a μ_3 -bridging O^{2-} at the center of the triangle, six acetate anions connecting the metal atoms *via* carboxylate oxygen atoms, reinforcing the triangular framework, and three terminal water molecules (Figure 1) [20,21]. The ferrites MFe_2O_4 were synthesized by sintering of $[\text{Fe}_2\text{M}(\mu_3\text{-O})(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Mn}^{\text{II}}$, Co^{II} , and Ni^{II}) at an appropriate temperature for 5 hours:

Thermogravimetric studies of the precursor complexes revealed that their thermal decomposition was complete at approximately 300°C [22]. An additional evidence of this is the disappearance of the bands associated with the acetate groups in the IR spectra of these samples. The elemental analysis and X-ray powder diffraction data (XRD) of samples annealed for 5 hours at 320°C revealed the formation of spinel phases MFe_2O_4 (Table 1 and Figure 2).

For the cobalt and nickel-containing samples calcined in the range from 320 to 600°C, reflections corresponding only to the cubic spinels were observed. In the case of the cobalt-containing samples, increasing the annealing temperature to 700°C led to the appearance of reflections characteristic of Fe_2O_3 and cobalt oxides formed as a result of oxidative

decomposition of CoFe_2O_4 . Similarly, thermal decomposition of $[\text{Fe}_2\text{Mn}(\mu_3\text{-O})(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\cdot 2\text{H}_2\text{O}$ at 320–400°C led to the formation of MnFe_2O_4 , but at higher temperatures its oxidation took place. XRD patterns of the samples obtained at 600 and 700°C showed no reflections corresponding to MnFe_2O_4 . Only peaks, characteristic for Mn_2O_3 and Fe_2O_3 were observed. Thus, the formation of pure MnFe_2O_4 from $[\text{Fe}_2\text{Mn}(\mu_3\text{-O})(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\cdot 2\text{H}_2\text{O}$ occurs in a relatively narrow temperature interval (320–400°C).

The nano-sized nature of the obtained ferrites leads to broadening of the XRD peaks. The average size of the nanocrystals was evaluated using Scherrer's method [23]; the results are presented in Table 1. In all cases, increasing the annealing temperature is accompanied by narrowing of the diffraction peaks due to an increase in the particles size as a result of the sintering, which also leads to an improvement in the crystallinity of the solids.

The nanoscale size of the ferrite crystals was also confirmed by transmission electron microscopy (TEM, Figure 3). The particle size measured from TEM photographs are consonant with those obtained from XRD data (Table 1).

The magnetic properties of samples annealed at 400° C were studied in a wide sub-ambient temperature range (Figures 4 and 5).

The field dependence of the magnetization of MnFe_2O_4 shows no hysteresis at 300 K, while at 10 K open hysteresis loop with coercivity (H_c) 600 Oe can be clearly observed. The value of the saturation magnetization (M_s) at 300 K is 55 emu/g and reaches 65 emu/g when the temperature is approaching to 10 K. There is no pronounced maximum on the temperature dependence of the magnetization in zero field cooled (ZFC) mode ($H=50$ Oe) but the magnetization substantially changes with the temperature variation (Figure 5). Meanwhile in the field cooled (FC, $H=50$ Oe) mode the magnetization remains practically constant within the studied temperature interval.

For the CoFe_2O_4 , a relatively narrow hysteresis loop is observed at 300 K, with $M_s = 83$ emu/g and $H_c = 1200$ Oe (Figure 4). At lower temperatures the hysteresis loop becomes much broader, with $M_s = 88$ emu/g and $H_c = 18500$ Oe at 10 K. Similarly to Mn ferrites, the FC curve does not show any appreciable temperature dependence of the magnetization (Figure 5). However in contrast with manganese ferrite, the ZFC curve for CoFe_2O_4 also does not show substantial variation of the magnetization with the temperature (Figure 5). There is no merging of the ZFC and FC curves even at 300 K.

The magnetization vs. magnetic field curve for NiFe_2O_4 at 300 K is completely reversible without any sign of hysteresis ($M_s = 45$ emu/g), while at 10 K, a narrow hysteresis loop appeared with $M_s = 56$ emu/g and $H_c = 650$ Oe (Figure 4). The magnetization of NiFe_2O_4 in FC mode slightly decreases with the temperature increase, while its temperature dependence in ZFC mode passes through a well-defined maximum at 220 K (Figure 5). The two curves converge at 275 K.

3. Discussion

Synthesis

Sintering of heterometallic trinuclear oxoacetates $[\text{Fe}_2\text{M}(\mu_3\text{-O})(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Mn}^{\text{II}}$, Co^{II} , and Ni^{II}) within the temperature interval 300–400°C resulted in their decomposition with formation of corresponding spinel-structured ferrites MFe_2O_4 according to equation (1). The reaction (1) is similar to the well-known Piria reaction commonly used for synthesis of organic carbonyl compounds [24]. Accordingly, the main products formed

from the radical-generating decarboxylation in (1) are acetone, carbon dioxide and water. Both elemental analyses (Fe and Mn content) and XRD of the powders obtained below 400°C showed the formation of pure ferrites MnFe_2O_4 with spinel structures. Therefore, the essential advantage of the proposed method for spinel formation from heterometallic trinuclear oxoacetates is the substantially decreased processing temperature compared to classical calcination procedures (~1000°C) [25–28].

The nanocrystals obtained within the optimum processing temperature range of 300–400°C have diameters of 7–20 nm. We consider certain factors to be important in the generation of nanoparticulate products. First, the gaseous thermolysis products promote efflorescence of the solid particles during synthesis, and consequently reduce their size. Second, the low thermolysis temperature reduces the degree of sintering, and inhibits the particle fusion that occurs at higher temperatures. At higher temperatures, indeed, we observed aggregation into larger particles, as well as oxidative instability of the Mn and Co ferrites.

The size distribution was obtained by statistical analysis of TEM images (Table 1). Table 2 summarizes the data on the size of the nanocrystals produced by different methods.

It might be noted that the morphology of the nanocrystals obtained in this work occupies an intermediate position in this scale. Therefore, the “polynuclear complex to nanoparticles” approach does not represent a universal method, but offers its advantages of simplicity and scalability of the process as well as high purity and homogeneity of the products.

Magnetic properties

For nanosized MnFe_2O_4 , the M_s value (55 emu/g) is significantly lower than for bulk MnFe_2O_4 (80 emu/g). This value is agree to obtained for similar size nanoparticles of MnFe_2O_4 (~53 emu/g for 13.5 nm) [14]. The reversible room temperature magnetization and narrow hysteresis loop at 10 K are typical for superparamagnets which behave below their blocking temperature (T_B) as ferrimagnetics, but above T_B show properties of classical paramagnets, with total spin equal to the spin of a whole particle. At T_B half the nanoparticles can overcome their anisotropy energy barrier. The M_r/M_s ratio MnFe_2O_4 at 10 K is 0.38, which is rather low in comparison with the theoretical value for particles with cubic magnetocrystalline anisotropy. The low value of M_r/M_s can be accounted for by the hysteresis properties of these ferrites at low temperature being mainly determined by their surface anisotropy, resulting from surface spin disorder (spin canting) rather than cubic anisotropy. The shift of the hysteresis loop to lower field after cooling is characteristic of such anisotropy. Furthermore, agglomeration of the particles leads to strong influence of dipole-dipole interaction among the particles, which usually results in a decrease of M_r/M_s value for materials with relatively low coercivity; the coercivity at 10 K is 600 Oe. The MnFe_2O_4 nanoparticles with average diameter 8 nm showed $H_c = 190$ Oe at 20 K [29], and MnFe_2O_4 nanoparticles with average size from 4 to 14 nm showed H_c from 30 to 300 Oe at 20 K [14]. This difference is associated with a difference in surface properties and shapes of particles prepared using different methods.

The T_B value can be extracted from the position of the maximum on zero field cooling (ZFC) magnetization curves. For MnFe_2O_4 the ZFC curve does not reach a maximum even by 300 K. However, the fact that no hysteresis was observed (for the magnetization vs. magnetic field) allows us to conclude that the maximum is close to 300 K. A $T_B = 150$ K was previously reported [29] for MnFe_2O_4 particles with $d \sim 8$ nm, and 250 K for particles with size 13.5 nm [14].

Taking the value of the blocking temperature T_B as 300 K, it is possible to estimate the value of the magnetic anisotropy constant K , as [30]:

$$KV=25kT_B \quad (2)$$

(k is the Boltzmann constant, V is the particle mean volume), which gives $K \sim 7 \times 10^5 \text{ erg cm}^{-3}$. The application of this equation to the data previously reported [29] for MnFe_2O_4 particles with $d \sim 8 \text{ nm}$ gives a K value of $2 \times 10^6 \text{ erg cm}^{-3}$, which is almost three times higher. Taking into consideration that the coercivity at low temperatures was about three times lower than for our manganese nanoferrites, the only possible explanation is that the value of the anisotropy constant for this nanomaterial is mainly determined by the surface properties of the particles rather than magnetocrystalline anisotropy [1,2]. Defects, non-saturated valences and broken bonds on the surface of nanospecies as well as a shape of the particles can lead to substantial variation in magnetic characteristics of nanoferrites [1,2]. It should be emphasized that the influence of surface properties becomes dominant for particles with low magnetocrystalline anisotropy.

The magnetic properties of the CoFe_2O_4 nanocrystallites with an average diameter of 11 nm substantially differ from those of manganese spinel. ZFS-FC do not superimpose up to 300 K and agree with data of paper [17] in which this observation was attributed to the presence of nanoparticles in ferromagnetic state at room temperature. Magnetic hysteresis was observed at 300 K in spite of the smaller size of the particles. Taking into account, that the value of the magnetocrystalline anisotropy for cobalt ferrites is at least an order of magnitude higher than the cobalt system, it is to be expected that this could be the case. However, it is worth noting that magnetic properties of Co ferrite particles also depend markedly on the preparation method. For instance, for CoFe_2O_4 particles with average diameter of 2–5 nm being dispersed in an inert matrix, no hysteresis was observed at 300 K [31]. Nevertheless, this property was seen at ambient temperature for CoFe_2O_4 particles with an average diameter of 5 nm in powder [31]. Therefore, the transition to the superparamagnetic state is determined not only by the chemical nature of the ferrite and the size of its particles, but also by the degree of structural imperfection and the morphology of its surface [32–34]. The higher 10 K coercivity value (18500 Oe) for our particles in comparison with the earlier report for Co ferrite nanocrystals of the same diameter (7500 Oe) [17] can be ascribed to the higher degree of their crystallinity of our preparations and the consequently greater magnetocrystalline anisotropy. Also increasing of H_C value can be the evidence of existing of strong magnetic interactions between nanoparticles [17,35]. The value of the saturation magnetization at 300 K (83 emu/g) is close to the calculated value of the bulk material [36] and significantly exceeds the value observed earlier for most of nanosize cobalt ferrites [37–38], also supporting the contention that our products are of good crystallinity. Recently high M_s value (76.2 emu/g) was reported for nano-sized cobalt(II) ferrite in [19,39]. The low M_r/M_s ratio at 300 K (0.28) as well as the fact that the coercivity value obtained is lower than for bulk material [36] implies that there is a fraction of particles which are superparamagnetic at room temperature. Decreasing the temperature results in an increase in the M_r/M_s ratio, which reaches 0.73 at 10 K. A dramatic increase of coercivity ($\sim 18500 \text{ Oe}$ at 10 K) is also observed. However this value of coercivity cannot be ascribed to magnetocrystalline anisotropy alone. Again, the characteristic shift of the hysteresis loop, when the sample was cooled down in the magnetic field, shows a substantial influence of surface anisotropy due to spin canting.

For the nickel ferrites ($d \sim 7 \text{ nm}$), no magnetization hysteresis was observed at room temperature but at 10 K there is hysteresis with $H_C \sim 650 \text{ Oe}$ with an M_r/M_s ratio of 0.24.

The ZFC curve has clear maximum at 225 K, corresponding to T_B . Both the ZFC and FC curves merge at $T_s \sim 250 \text{ K}$ (this value, in contrast to T_B , reflects the temperature, at which

all the magnetic particles attain the superparamagnetic state [40]). Approximately the same T_s was reported previously for NiFe_2O_4 nanoparticles with a larger d (10 nm), while the ZFC curve maximum was observed below 100K [41]. Increasing particle size usually results in an increase in the T_B value, instead of the observed decrease; again, the only reasonable accounting for this falls to the different properties of the particle surfaces.

The blocking temperature is thus in each case determined by a delicate balance among several factors: spin-orbit interaction in M^{2+} , Fe^{3+} ions, particle size and properties of the nanoparticle surface. Also, within nanocrystallites of identical size there can be a different population of sites A (tetrahedral) and B (octahedral) by M^{2+} and Fe^{3+} and ions in these two different site symmetries exhibit different spin-orbit couplings [35]. In terms of their blocking temperatures the spinels investigated in this study follow the order: $\text{CoFe}_2\text{O}_4 > \text{MnFe}_2\text{O}_4 > \text{NiFe}_2\text{O}_4$. Site population, particle size and surface defect properties all contribute inextricably to this ranking.

4. Conclusions

A new method of production of nano-sized ferrites by thermal decomposition of single-molecule heteropolynuclear precursors was developed. It was demonstrated that thermal decomposition of trinuclear heterometallic oxoacetates $[\text{Fe}_2\text{M}(\mu_3\text{-O})(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Mn}^{\text{II}}$, Co^{II} , and Ni^{II}) in the 400–700°C range resulted in formation of appropriate MFe_2O_4 nanospecies. Increasing the reaction temperature led to enlargement of particle size. The proposed method can be applied to synthesis of various heterometallic oxides with different metal(A)/metal(B) ratio depending on the composition of the polynuclear skeleton in single molecule precursor. The approach also promises high purity and homogeneity of desired nano products.

The Ni and Mn nanospinels obtained evidenced superparamagnetic behavior while CoFe_2O_4 displayed ferromagnetic properties. Comparison of their magnetic properties with those from the literature showed that magnetic characteristics of nanospinels are determined not only by their particle size but are also influenced by a delicate balance among several factors: spin-orbit interaction in constituent metal ions, particle size and properties of the nanoparticle surface.

5. Experimental Section

Commercially available reagents (Ukreahim, Aldrich) were used as received. Polynuclear precursors $[\text{Fe}_2\text{M}(\mu_3\text{-O})(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Mn}^{\text{II}}$, Co^{II} , and Ni^{II}) were prepared as described [20,22]. Appropriate spinels were synthesized by their thermolysis in oven under the aerobic conditions. Metal content was estimated using a KAS-10 atomic absorbance analyzer (SELMi, Ukraine). XRD was performed on DRON-3M diffractometer (NPO Boorevestnik, USSR) ($\text{Cu K}\alpha$ radiation). Transmission electron microscopy (TEM) images were obtained on a JEOL 2010 instrument. Magnetic measurements were done using a Quantum Design MPMS SQUID magnetometer.

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References

1. Kodama HRH, Berkowitz AE, McNiff EJJ, Foner S. J Appl Phys. 1997; 81:5552.
2. Muroi M, Street R, McCormick PG. Phys Rev B. 2001; 63:184414.
3. O'Brien S, Brus L, Murray CB. J Am Chem Soc. 2001; 123:12085. [PubMed: 11724617]
4. Wang J, Chen Q, Hou B, Peng Z. Eur J Inorg Chem. 2004:1165.
5. Li F, Liu J, Evans D, Duan X. Chem Mater. 2004; 16:1597.
6. Rohrer H. Microelectron Engin. 1996; 32:5.
7. White RL. J Magn Magn Mater. 2000; 209:1.
8. Fröba M, Reller A. Prog Solid St Chem. 1999; 27:1.
9. Philippov, VI.; Vladimirkii, MA.; Androsova, MV.; Dobrinskii, EK. Russian Patent. 2140084. 1999.
10. Vestal CR, Zhang ZJ. Chem Mater. 2002; 14:3817.
11. Torres F, Asenjo AJ, Krotenko AJ, Tejada J, Brillas E. Chem Mater. 2000; 12:3060.
12. Li L, Li G, Smith RLJ, Inomata H. Chem Mater. 2000; 12:3705.
13. Yu SH, Yoshimura M. Chem Mater. 2000; 12:3805.
14. Liu C, Zhang ZJ. Chem Mater. 2001; 13:2092.
15. Jia X, Chen D, Jiao X, He T, Wang H, Jiang W. J Phys Chem C. 2008; 112:911.
16. Gu Z, Xiang X, Fan G, Li F. J Phys Chem C. 2008; 112:18459.
17. Cannas C, Ardu A, Musinu A, Peddis D, Piccaluga G. Chem Mater. 2008; 20:6364.
18. Nyutu EK, Conner WC, Auerbach SM, Chen CH, Suib SL. J Phys Chem C. 2008; 112:1407.
19. Wang Z, Liu X, Lv M, Chai P, Liu Y, Zhou X, Meng J. J Phys Chem C. 2008; 112:15171.
20. Blake AB, Yavari A, Hatfield WE, Sethulekshimi CN. J Chem Soc, Dalton Trans. 1985:2509.
21. Gavrilenko KS, Vertes A, Vanko G, Kiss LF, Addison AW, Weyhermüller T, Pavlishchuk VV. Eur J Inorg Chem. 2002:3347.
22. Gavrilenko, KS.; Mironyuk, TV.; Il'in, VG.; Orlik, SN.; Pavlishchuk, VV. Theor Eksp Khim (Rus Ed). Vol. 38. 2002. p. 110
23. Hammond, C. The Basics of Crystallography and Diffraction. Oxford University Press; Oxford: 1997.
24. Piria R. Liebig's Ann Chem. 1856; 100:105.
25. Bergemann C, Muller-Schulte D, Oster J, Brassard L, Lubbe AS. J Magn Magn Mater. 1999; 194:45.
26. Ding J, Reynolds T, Miao WF, McCormick PG, Street R. Appl Phys Lett. 1994; 65:3135.
27. Rajendran MR, Pullar C, Bhattacharya AK, Das D, Chintalapudi SN, Majumdar CK. J Magn Magn Mater. 2001; 232:71.
28. Moumen N, Pileni MP. J Phys Chem. 1996; 100:1867.
29. Roger J, Pons JN, Massart R, Halbreich A, Bacri JC. Eur J Phys Appl Phys. 1991; 5:321.
30. Leslie-Pelecky DL, Rieke RD. Chem Mater. 1996; 8:1770.
31. Moumen N, Pileni MP. Chem Mater. 1996; 8:1128.
32. Liu N, Zou B, Rondinone AJ, Zhang ZJ. J Am Chem Soc. 2000; 122:6263.
33. Jiles, D. Introduction to Magnetism and Magnetic Materials. Chapman and Hall; London: 1991.
34. Unruh, KM.; Chien, CL. Nanomaterials: Synthesis, Properties and Applications. Institute of Physics Publishing; Bristol: 1996.
35. Liu C, Zou B, Rondinone AJ, Zhang ZJ. J Phys Chem B. 2000; 104:1141.
36. Enz, U.; Zijlstra, H.; McCurrie, RA.; Krupicka, S.; Novak, P.; Kojima, H.; Sugimoto, M.; Stablein, H.; van Stapele, RP.; Campbell, IA.; Fert, A. Ferromagnetic Materials. Wohlfarth, EP., editor. Vol. 3. North Holland Publishing Co; Amsterdam: 1982. p. 852
37. Shafi KVPM, Gedanken A, Prozorov R, Balogh J. Chem Mater. 1998; 10:3445.
38. Yan CH, Xu ZG, Cheng FX, Wang ZM, Sun LD, Liao CS, Jia JT. Solid State Commun. 1999; 111:287.

39. Bensebaa F, Zavaliche F, L'Ecuyer P, Cochrane RW, Veres T. *Journal of Colloid and Interface Science*. 2004; 277:104. [PubMed: 15276045]
40. Pérez JAL, Quintela MAL, Mira J, Rivas J, Charles SW. *J Phys Chem B*. 1997; 101:8045.
41. Shi Y, Ding J, Shen ZX, Sun WX, Wang L. *Solid State Commun*. 2000; 115:237.
42. Carantu D, Remond Y, Chou NH, Jun MJ, Carantu G, He J, Goloverda G, O'Connor C, Kolesnichenko V. *Inorg Chem*. 2002; 41:6137. [PubMed: 12425644]
43. Joy PA, Date SK. *J Magn Magn Mater*. 2000; 210:31.
44. Sousa MH, Tourihno FA, Depeyrot J, da Silva GJ, Lara MCFL. *J Phys Chem B*. 2001; 105:1168.
45. Gautam UK, Ghosh M, Rajamathi M, Seshadri R. *Pure Appl Chem*. 2001; 74:1643.

Figure 1.
Molecular structure of the precursor complexes $[\text{Fe}_2\text{M}(\mu_3\text{-O})(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Mn}^{\text{II}}, \text{Co}^{\text{II}}, \text{and Ni}^{\text{II}}$)

Figure 2.

Typical X-ray diffraction pattern for Mn, Co and Ni ferrites synthesized by sintering of heterometallic trinuclear oxo-acetate complexes $[\text{Fe}_2\text{M}(\mu_3\text{-O})(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Mn}^{\text{II}}$, Co^{II} , and Ni^{II}).

Figure 3.
TEM image for CoFe₂O₄ nanocrystals.

Figure 4.
 M vs H curves of spinels at 300 and 10 K: a - MnFe_2O_4 ; b - CoFe_2O_4 ; c - NiFe_2O_4 .

Figure 5. Zero field cooling and field cooling (50 Oe) magnetization curves of spinels: a - MnFe_2O_4 ; b - CoFe_2O_4 ; c - NiFe_2O_4 .

Table 1

Composition and metrics (from XRD data) of nanoparticles obtained from $[\text{Fe}_2\text{MO}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\cdot 2\text{H}_2\text{O}$ at different annealing temperatures.

Complex	Temperature, °C	Phases	Particle size, Å
$[\text{Fe}_2\text{MnO}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\cdot 2\text{H}_2\text{O}$	320	MnFe_2O_4	80
	400	MnFe_2O_4	150
	600–700	Mn_2O_3 , Fe_2O_3	-
$[\text{Fe}_2\text{CoO}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\cdot 2\text{H}_2\text{O}$	320	CoFe_2O_4	80
	400	CoFe_2O_4	80
	600	CoFe_2O_4	220
	700	CoFe_2O_4 , Fe_2O_3	270
$[\text{Fe}_2\text{NiO}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\cdot 2\text{H}_2\text{O}$	320	NiFe_2O_4	100
	400	NiFe_2O_4	90
	600	NiFe_2O_4	270
	700	NiFe_2O_4	340

Table 2

Methods of preparation and spinel nanoparticles size.

Compound	D_{av} , nm	Method of preparation	Refence
MnFe ₂ O ₄	6.6 ^b	non-aqueous solution hydrolysis of chelated complexes	42
MnFe ₂ O ₄	4–14	micellar	14
MnFe ₂ O ₄	14	annealing of heteromettalic polynuclear complex	this work
CoFe ₂ O ₄	< 5	sonochemical	37
CoFe ₂ O ₄	6–20 ^c	precipitation with NaOH in the presence of H ₂ O ₂	43
CoFe ₂ O ₄	4–85 ^d	combustion with further calcination at 400° !	38
CoFe ₂ O ₄	2–5	micellar	28
CoFe ₂ O ₄	20	micellar	32
CoFe ₂ O ₄	5.5	polyol medium	38
CoFe ₂ O ₄	4.0 ^a ; 3.3 ^b	non-aqueous solution hydrolysis of chelated complexes	42
CoFe ₂ O ₄	8.4	hydrothermal coprecipitation	44
CoFe ₂ O ₄	7	Co(II) and Fe(III) complexes with cupferon in the presence of octylamine	45
CoFe ₂ O ₄	11	annealing of heteromettalic polynuclear complex	this work
NiFe ₂ O ₄	3.6 ^b	non-aqueous solution hydrolysis of chelated complexes	42
NiFe ₂ O ₄	10	mechanical milling with subsequent annealing at 600° !	41
NiFe ₂ O ₄	4.4	hydrothermal coprecipitation	44
NiFe ₂ O ₄		annealing of heteromettalic polynuclear complex	this work

^a obtained at room temperature.^b obtained by elevated temperature method.^c depending on annealing temperature.^d depending on glycine concentration in pre-ignited mixture.