Some aspects of nanocrystalline nickel and zinc ferrites processed using microemulsion technique

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Nanocrystalline nickel and zinc ferrites synthesised using a microemulsion technique were characterised by high resolution transmission electron microscopy and vibrating sample magnetometry. A narrow and uniform distribution of crystals of size range 5–8 nm, distinguished by a clear lack of saturation magnetisation at 9 kOe, were obtained. Also, no coercivity or remanence was observed. **MST/5813**

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Introduction

The development of nanocrystalline materials is a subject of considerable interest, both for the scientific value of understanding the unique properties of materials that have relevance to condensed matter studies, and for the technological significance of enhancing the performance of existing materials. The ability to produce nanocrystalline ferrites is expected to assist in controlling the ultimate properties of ferrites, an advantage over those fabricated by powder metallurgy process. The magnetic properties, in particular, are strongly dependent on crystallite size, crystallite size distribution, and morphology of crystallites.

High electrical resistance and lower saturation magnetisation are the characteristics of soft ferrites, which are not found in traditional silicon steels and permalloys.[1] This makes them suitable for varied applications, including magnetic and magneto-optical. Modern data storage applications require control over the morphology of particles and a considerable reduction in crystallite size, to the size of a domain. Nanosize magnetic materials are expected to prove very useful in such applications. In recent years, a number of chemical and physical methods have been attempted to produce nanosize ferrites. Some of the main physical methods include mechanical milling,[1–4] severe plastic deformation consolidation,[5] and inert gas condensation.[6] The widely used chemical methods are electrodeposition,[7] hydrothermal reaction,[8] oxidative precipitation,[9] the organic precursor method,[10] sonochemical decomposition,[11] and the sol–gel synthesis technique.[12] The majority of these methods suffer from a lack of control of particle size distribution. The water in oil microemulsion chemical synthesis method permits a narrow size distribution of nanocrystalline particles to be obtained. It also has the advantage of simple equipment and operating conditions. In the water in oil emulsion system, the small droplets of water that are encapsulated into reverse micelles act as microreactors, providing a microstructured system to produce well defined nanosized crystallites[13] (micelle: a colloidal aggregate of amphiphilic surfactant molecules such that the hydrophobic ends are in contact; reverse micelle: a colloidal aggregate of amphiphilic surfactant molecules whereby hydrophilic ends are in contact). The size of nanocrystallites depends on the size of water pools and the water content. Thus, the success of this method depends on the surfactant and solvent used, amount of water in the system, and concentration of surfactant. In the present paper, the potential of the water in oil microemulsion method for producing nanocrystalline ferrites is described, and the initial observations of high resolution transmission electron microscopy and magnetic measurements are outlined.

Experimental procedure

Nanocrystalline nickel and zinc ferrites based on the reverse micelle concept were synthesised using two microemulsion systems. The first microemulsion system was an oil phase microemulsion comprising iso-octane and surfactant sodium diiso-octylsulphoccinate (AOT); the second microemulsion was an aqueous phase emulsion consisting of iso-octane and surfactant diiso-octylsulphoccinate with reactant salts (hydrated iron sulphate and hydrated nickel sulphate or zinc sulphate, depending on the nature of the ferrite being processed). The $[Fe^{2+}]/[Ni^{2+}]$ or $[Fe^{2+}]/[Zn^{2+}]$ ratio in the metal containing solution was 2:1. In a typical experiment for the synthesis of nickel ferrite, microemulsion I consisted of 2 mL of 30% ammonium hydroxide + 2·4 mL of water + 66 mL of 0·5M AOT – iso-octane, and microemulsion II contained 0·384 g of $FeSO_4.7H_2O + 0·192$ g of $NiSO_4.6H_2O + 66$ mL of 0·5M AOT – iso-octane. The constitution of microemulsion systems for the processing of zinc ferrites was identical to that for nickel ferrites except for the replacement of nickel sulphate in microemulsion II by zinc sulphate. Ammonium hydroxide acted as a precipitating agent to form metal hydroxides. Ammonium hydroxide also provided stability to the water in oil system. The two microemulsions were mixed and subjected to rapid mechanical stirring. In initial experiments for the synthesis of nickel ferrites, the mechanical stirring time was 10 min. However, this led to the synthesis of amorphous nickel ferrites (*see* below). The time was then increased to 15, 25, 50 min. The optimum mechanical stirring time required to produce nanocrystalline ferrites was determined to be 25 min. This duration was used for subsequent experiments. Hydroxides of nickel and iron were precipitated within the water pools of reverse micelles and subsequently oxidised to nickel ferrite. This was followed by separation of the solid product by a centrifuging process. The resulting solid
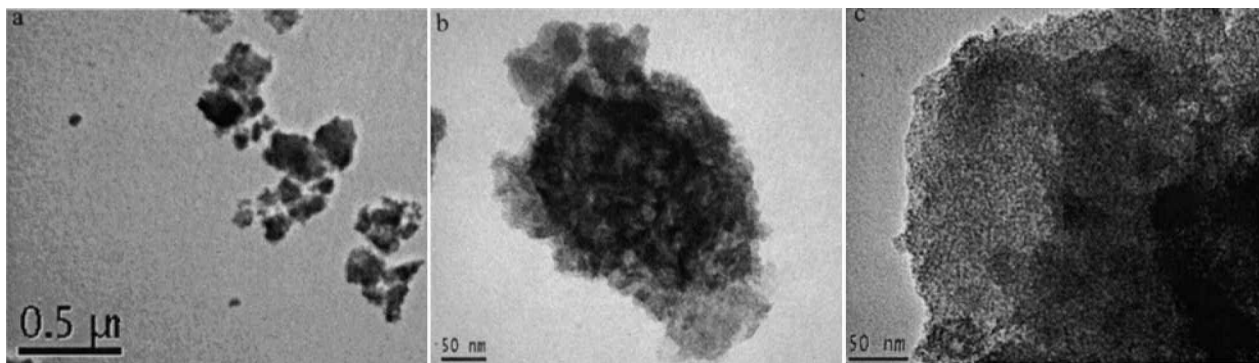
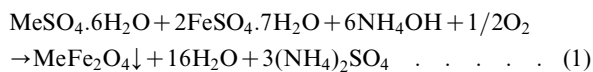*a* lower magnification; *b,c* higher magnification

1   Images (TEM) at different magnifications of amorphous nickel ferrite powder produced by inadequate mechanical stirring (10 min) of microemulsion systems

product was washed a number of times with methanol followed by drying in a low vacuum. The chemicals used for synthesis of nanocrystalline ferrite were of analytical grade, obtained from Aldrich, and the water used was doubly distilled.

The ferrites were characterised by transmission electron microscopy (TEM) to determine crystallinity, extent of segregation of the nanoparticles, and their particle size (distribution). The TEM samples were prepared as follows. Ferrite powder was pulverised and dispersed in isopropyl alcohol, and a droplet of the suspension was put on a carbon or formvar coated copper grid located on a glass slide. After drying, the grids were inserted in the microscope. A Jeol 4000 EX/II operating at 400 kV having a point–point resolution of 0·165 nm, and a Jeol 2010FEG (field emission gun) operating at 200 kV having an information limit of 0·11 nm, equipped with an EDAX EDS detector (with super ultrathin window), were used. *In situ* heating was carried out in the Jeol 2010FEG using a Gaton double tilt heating holder (model 652 with a model 901 SmartSet hot stage controller). Magnetic measurements were conducted at room temperature using a vibrating sample magnetometer with an applied field of 9 kOe.

Results and discussion

The anticipated chemical reaction expected to produce nickel and zinc ferrite is

$$MeSO_4.6H_2O + 2FeSO_4.7H_2O + 6NH_4OH + 1/2O_2$$
$$\rightarrow MeFe_2O_4\downarrow + 16H_2O + 3(NH_4)_2SO_4 \quad . \quad . \quad . \quad . \quad (1)$$

where $Me = Ni$ or Zn.

The first observation was that the mechanical stirring time of the microemulsion was critical for the synthesis of nanocrystalline ferrites. As stated above, mechanical stirring for less than the critical time of 25 min produced amorphous ferrites. Micrographs (TEM) of nickel ferrites produced by mechanical stirring of the two microemulsion systems for 10 min are presented in Fig. 1, confirming the amorphous nature of the nickel ferrites. Figure 1 gives no evidence of crystallite formation, and particles are seen to be aggregated. The amorphous nickel ferrites were heat treated *in situ* in the microscope at 500, 600, and 700°C for 5 min, and the progress in crystallisation of the amorphous ferrites was examined. Figures 2–4 clearly indicate that amorphous nickel ferrites transform to nanocrystalline nickel ferrites. Following heat treatment at 500°C for 5 min, nickel ferrite crystals of 5–10 nm could be seen (Fig. 2*b*). However, the heat treatment time of 5 min was not adequate for complete transformation of amorphous nickel ferrites to nanocrystalline ferrites, and the selected area diffraction pattern predominantly indicated diffuse rings characteristic of an amorphous nature (Fig. 2*c*). After heat treatment at 600°C for 5 min, crystallisation was promoted, and a number of crystals could be seen (Fig. 3*a*) and the diffraction pattern (Fig. 3*b*) was representative of a crystalline material. Heat treatment at 700°C for 5 min led to complete crystallisation of the amorphous material, but at the same time the temperature was sufficiently high to promote crystal growth (Fig. 4). Several lines, namely [220], [311], [400], [511], and [440] could be identified in the diffraction pattern (Figs. 3*b* and 4*b*). Their positions and relative intensities confirm unambiguously the spinel crystallographic structure. The observed behaviour at different temperatures suggests that 500°C is adequate for transformation of an amorphous to a crystalline nature; however, a heat treatment time of greater
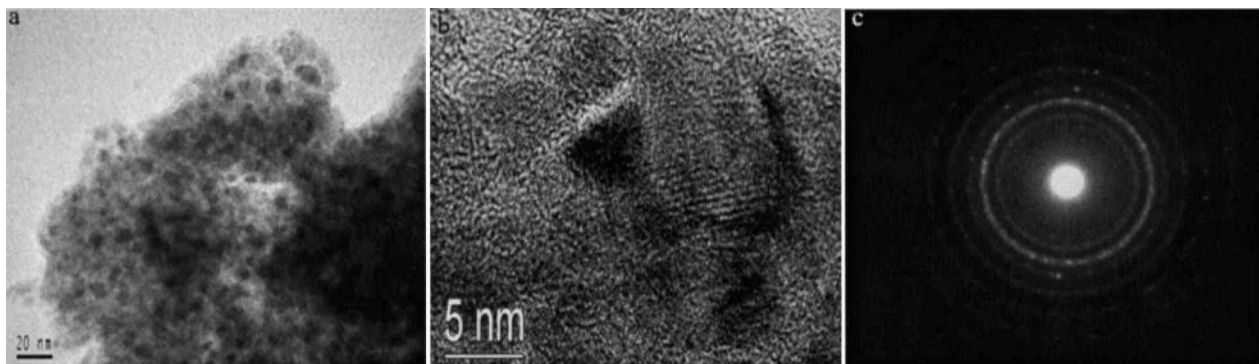
a,b TEM images; *c* SADP

2   Images (TEM) and selected area diffraction pattern (SADP) of amorphous nickel ferrite powder heat treated *in situ* in TEM at 500°C for 5 min
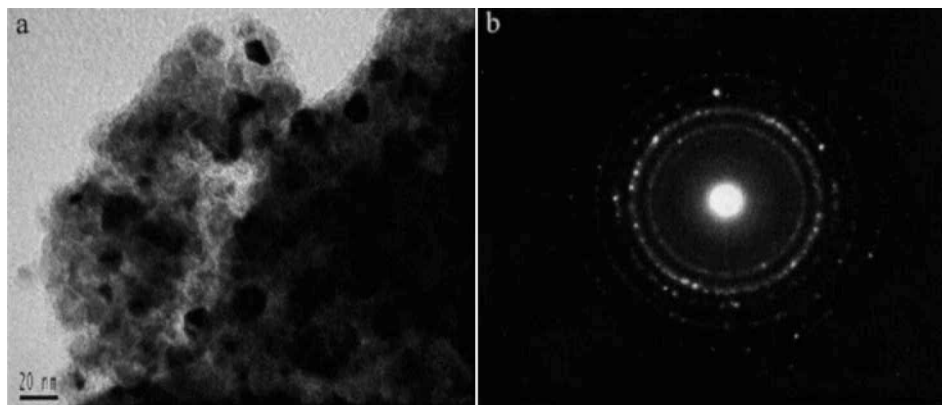
a TEM image; *b* SADP

3 Image (TEM) and selected area diffraction pattern (SADP) of amorphous nickel ferrite powder heat treated *in situ* in TEM at 600°C for 5 min

a TEM image; *b,c* SADPs

4 Image (TEM) and diffraction patterns (SADPs) of amorphous nickel ferrite powder heat treated *in situ* in TEM at 700°C for 5 min

than 5 min (10 min) is required for transformation to be complete.

Micrographs (TEM) of nanocrystalline nickel ferrites processed by mechanical stirring of the two microemulsions for 25 min are presented in Fig. 5. According to Fig. 5*a*, the particles were approximately spherical with a crystallite size of 5–8 nm (Fig. 5*b*), and the rings on the diffraction pattern depicted a spinel crystal structure of nickel ferrite. Several lines ([220], [311], [400], [511], and [440]) could be identified in the diffraction pattern in a manner similar to Figs. 3*b* and 4*b*. Their positions and intensities again confirm unambiguously the spinel structure. The

narrow distribution of crystallite size may be noted from Fig. 5*a*.

Considering that the nucleation and growth of billions of ferrite particles in a microreactor system requires a finite time for the chemical reaction to occur by a content exchange mechanism, involving the transfer of reactants following coalescence of a pair of reverse micelles, or owing to diffusion of the contents,[13] it is not surprising that an optimal mechanical stirring time is required to obtain nanocrystalline ferrites.

In line with the need for a critical time, zinc ferrites were processed in a manner similar to that for nanocrystalline
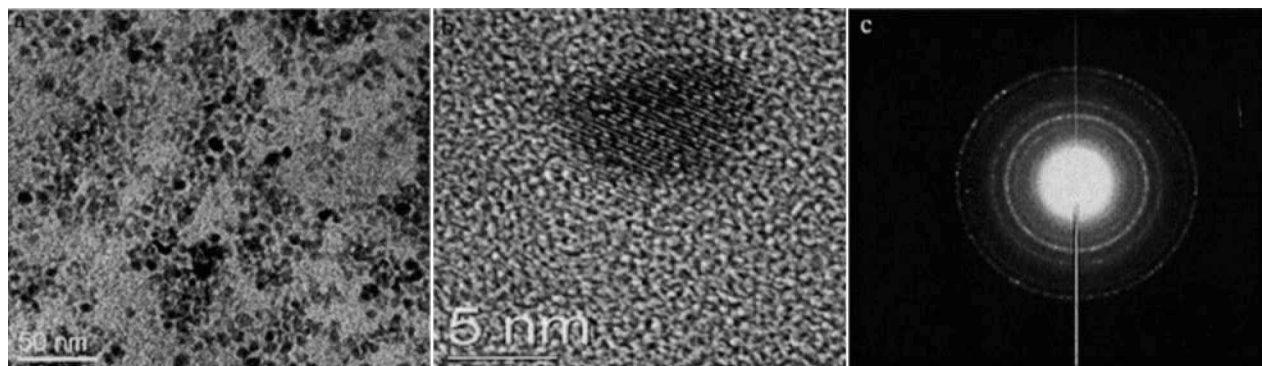
a,b TEM images; *c* SADP

5 Low and high magnification TEM images and diffraction pattern (SADP) of nanocrystalline nickel ferrite processed by mechanical stirring microemulsion for 25 min
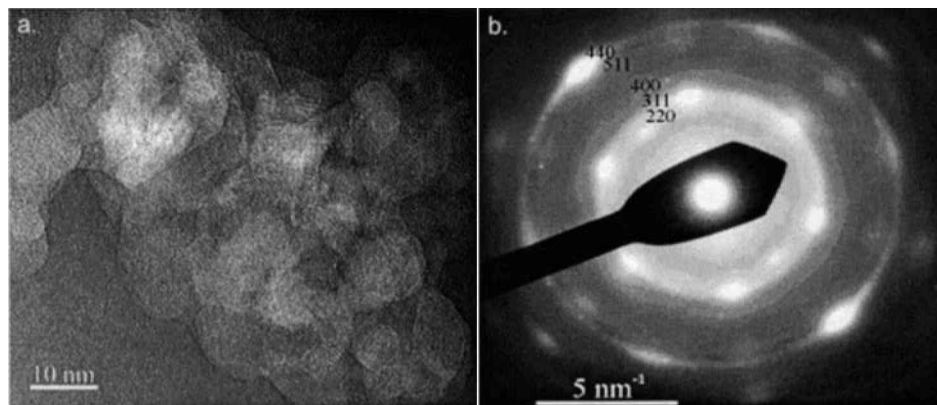
a TEM image; *b* SADP

6 Image (TEM) of nanocrystalline zinc ferrite and corresponding selected area diffraction pattern (SADP)

nickel ferrites using a mechanical stirring time of 25 min or greater. A TEM image of zinc ferrite and corresponding selected area electron diffraction pattern are presented in Fig. 6. The TEM image (Fig. 6*a*) indicates that there was some tendency for the particles to aggregate. The tendency for agglomeration depends on the water/surfactant molar ratio,[13] and was ($w = $[H$_2$O]/[surfactant]) 10 in the present experiment. This agglomeration can be minimised by minimising the water content/surfactant ratio. The diffraction pattern (Fig. 6*b*) was again characteristic of the spinel structure of zinc ferrite. Several lines, [220], [311], [400], [511], and [440], could be identified, similar to the case of nickel ferrite. Their position and relative intensities again confirm unambiguously the spinel crystallographic structure.

Quantitative analysis of the EDS spectra taken for some particles yielded an approximate stoichiometry of nickel and zinc ferrite of Ni$_x$Fe$_{3-x}$O$_4$/Zn$_x$Fe$_{3-x}$O$_4$ ($x \approx 1\cdot3$, $1\cdot2 \pm$

$0\cdot2$), implying that the concentration of nickel and zinc in the resultant ferrite was close to the stoichiometric composition.
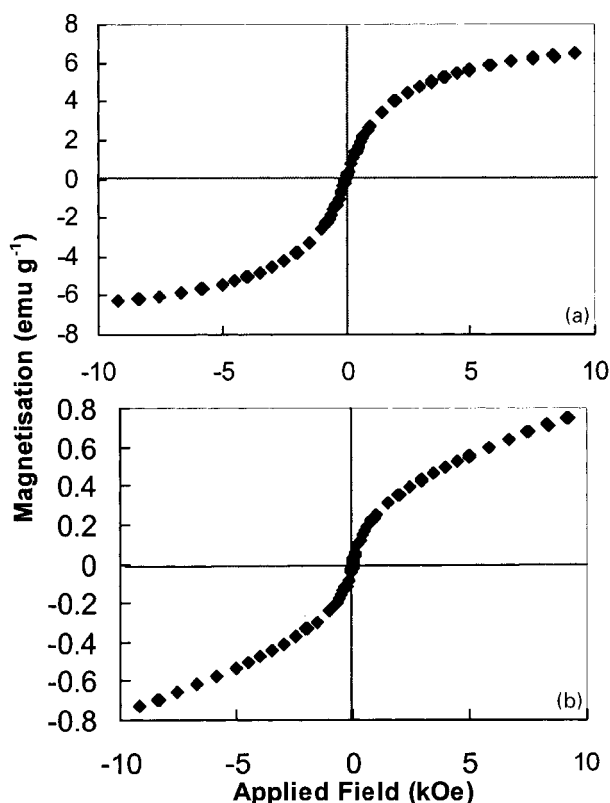
Initial magnetic measurements conducted at room temperature on powder samples seemed to suggest that the particles had a single domain structure and were superparamagnetic. Representative plots of magnetisation as a function of applied field are presented in Fig. 7 for nanocrystalline nickel and zinc ferrites. The magnetisation–field plot shows no hysteresis, and the higher field part does not indicate any real saturation. Even at 9 kOe, there is visible lack of saturation. The maximum observed value of magnetisation (6 emu g^{-1} for nickel ferrite, $0\cdot75$ emu g^{-1} at an applied field of 9 kOe for zinc nanocrystalline ferrite) is significantly lower than that of multidomain bulk particles. Almost no coercivity or remanence is observed. The low value of saturation magnetisation is attributed to the superparamagnetic nature of nickel and zinc ferrite, and to the non-collinearity of the magnetic moments at or near the surface of the particle. Nickel and cobalt ferrites, which also show a ferromagnetic inverse spinel, are known to have a non-collinear spin structure when they are present as fine crystallites.[14] The non-collinear structure attributed to a surface effect is more pronounced for a smaller crystallite size of nickel and zinc ferrite (<10 nm). Detailed magnetic studies are in progress.

Conclusions

Nanocrystalline nickel and zinc ferrites synthesised by a microemulsion method exhibited a crystallite size of about $5-10$ nm and an approximate stoichiometry of Me$_x$Fe$_{3-x}$O$_4$ (Me $=$ Ni or Zn) ($x \approx 1\cdot3$, $1\cdot2 \pm 0\cdot2$). They lacked saturation magnetisation at 9 kOe. A clear lack of coercive force and lack of remanence was also observed.

a nickel ferrite; *b* zinc ferrite

7 Magnetisation versus applied field for nanocrystalline nickel and zinc ferrite at 293 K

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